59. Synthesis of Unsubstituted and 4,4′-Substituted Oligobipyridines as Ligand Strands for Helicate Self-Assembly

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A general strategy for the synthesis of oligobipyridine ligands **2**–**5** containing from two to five 2,2′-bipyridine subunits, for helical metal complexes is described (see *Scheme*). Both the unsubstituted parent strands (**a** series) as well as their derivatives bearing ester or amide functions in the 4,4′-positions of the bipyridine moieties (**b**–**d** series) have been obtained.

1. Introduction. – Self-organisation consists of the spontaneous generation of well-defined supramolecular architectures by self-assembly from their components in a given set of conditions. The design of systems undergoing self-organisation represents a major goal of supramolecular chemistry [1]. We have pursued several approaches involving either metal-ion complexation or molecular recognition between complementary units as binding interactions [1]. In particular, self-organisation may occur in chain ligands containing several identical subunits, if successive binding of a given substrate to the different sites gives rise to a well-defined final structure.

This has been shown to occur in the case of the spontaneous formation of double helical metal complexes, the helicates, in which two oligobipyridine strands are wrapped helically around Cu^{I} or Ag^{I} metal cations which hold them together. Di- to pentahelicate complexes, in which two to five ions are bound, have thus been obtained [2–5].

To this end, oligobipyridine ligands containing two to five 2,2′-bipyridine (bpy) units have been synthesised. Furthermore, in order to allow the attachment of various residues to the oligobipyridine ligands and to the helicates, it becomes necessary to introduce functional groups onto the bpy units. This has been realised in the deoxyribonucleohelicates DNH which represent positively charged, inside-out analogues of the nucleic-acid double helix [5].

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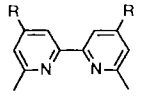
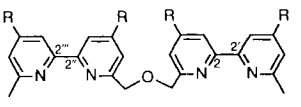
The key to the study of the helicate self-organisation processes and to the design of substituted derivatives bearing functionally active (redox active, photoactive, *etc.*) units, is the synthesis of the basic oligobipyridine strands. We describe here in detail the synthetic procedures towards the parent unsubstituted strands as well as the strands containing a 4,4′-disubstitution pattern on the bpy components.

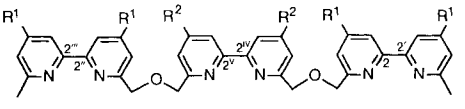
2. Target Molecules and Synthetic Strategy. – The 6,6′-oxybis(methylene)-linked oligobipyridines **2–5** containing two, three, four, and five 2,2′-bipyridine units were chosen as target molecules. The unsubstituted substances **2a**, **3a**, **4a**, and **5a** form the parent species. Inspection of molecular models based on the X-ray structure of the unsubstituted trimer helicate $[Cu_3(\mathbf{3a})_2](TfO)_3$ ($TfO = CF_3SO_3^-$) [2] showed that functional groups in the 4,4′-position of the bipyridines should be well suited for attaching various molecular fragments to the helicate structure and to organise them in a double-helical



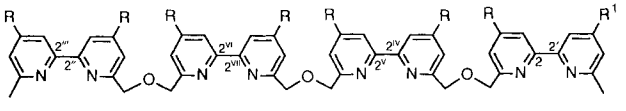
1a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$



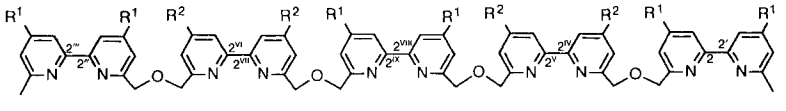
2a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$



3a $R^1 = R^2 = H$
b $R^1 = R^2 = CO_2(t\text{-Bu})$
c $R^1 = R^2 = CONEt_2$
d $R^1 = CH_2CH_2CO_2(t\text{-Bu})$, $R^2 = H$
e $R^1 = R^2 = CH_2CH_2CO_2(t\text{-Bu})$



4a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$

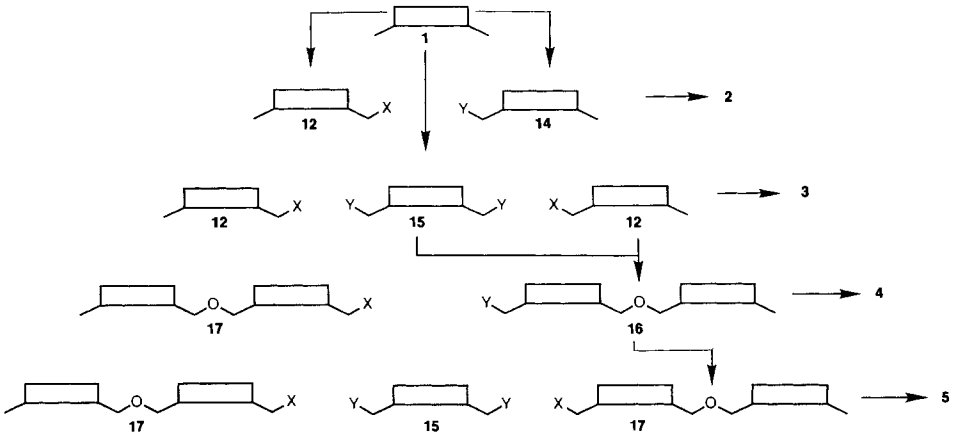


5a $R^1 = R^2 = H$
b $R^1 = R^2 = CO_2(t\text{-Bu})$
c $R^1 = R^2 = CONEt_2$
d $R^1 = CH_2CH_2CO_2(t\text{-Bu})$, $R^2 = H$

fashion. To this end, carboxy groups have now been introduced to give substituted strands bearing either ester or amide functions: **2b**, **3b**, **4b**, and **5b** and **2c**, **3c**, **4c**, and **5c**. Because of potential steric interactions between substituents that could occur on helicate formation, the trimeric and pentameric strands **3d** and **5d** containing alternatively substituted and unsubstituted bpy groups were also synthesised.

The general strategy followed was based on sequential *Williamson* condensations between functionalised components according to the schematic representation shown in the *Scheme*. As seen, the overall layout was convergent and the condensations involving a difunctional reagent made use of the (dibromide + 2 monoalcohol) rather than the (dialcohol + 2 monobromide) reaction. This choice was made in order to avoid having to generate a dialcoholate for the condensations.

Scheme. *Schematic Representation of the* Williamson *Condensations Leading to the Oligobipyridine Strands* **2**–**5** *Containing 2, 3, 4, and 5 Bipyridine Units.* Dimer **16** was obtained by condensing monomer dibromide **15** with monomer monoalcohol **12**, and dimer monoalcohol **17** was obtained by substituting the Br-atom in **16** by OH.

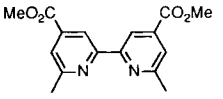


□ = 2,2′-bipyridine moiety, X = OH, Y = Br.

Extension of this scheme using, *e.g.*, difunctional dimeric components would allow the synthesis of the hexameric analogue and longer ones if desired, for exploring further the ion-binding features of oligomeric bipyridine strands. Furthermore, by using differently substituted bpy units or even different types of bi[heterocyclic (or other) units], mixed oligo(bpy) ligands may be synthesised. Of course, other reactions may be used for connecting the bpy groups, thus leading to different linkages between the subunits[6]).

3. Procedures and Results. 3.1. *Functionalised Mono- and Bis[bipyridines].* The substituted dimethylbipyridines **1b**–**d** were synthesised from the known diester **6** [8]. Thus, transesterification of dimethyl ester **6** with LiO(*t*-Bu) in *t*-BuOH/toluene [9] yielded di(*tert*-butyl)ester **1b** in 90% yield. Reaction of **6** with $Et_2NH/AlCl_3$ gave dicarboxamide **1c** in 96% yield, and reduction of **6** with $LiAlH_4$ afforded diol **7a** in 95% yield. *Swern*

[6]) This has been done using, *e.g.*, *Wittig* condensation [6] or oxidative coupling [7] reactions.



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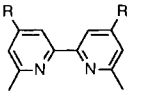
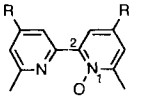
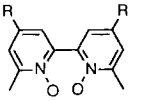


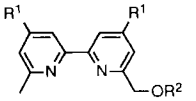
7a R = CH_2OH
b R = CHO
c R = $CH{=}CHCO_2(t\text{-Bu})$



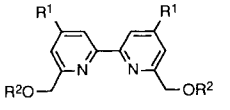
8a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$



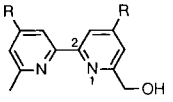
9a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$



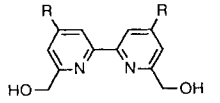
10a R^1 = H, R^2 = Ac
b $R^1 = CO_2(t\text{-Bu})$, $R^2 = COCF_3$
c $R^1 = CONEt_2$, $R^2 = COCF_3$
d $R^1 = CH_2CH_2CO_2(t\text{-Bu})$, R^2 = Ac



11a R^1 = H, R^2 = Ac
b $R^1 = CO_2(t\text{-Bu})$, $R^2 = COCF_3$
c $R^1 = CONEt_2$, $R^2 = COCF_3$
d $R^1 = CH_2CH_2CO_2(t\text{-Bu})$, R^2 = Ac



12a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$



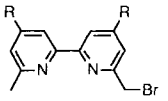
13a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$

oxidation [10] (83%) and *Wittig* reaction (80%) yielded diacrylate **7c**, and hydrogenation with Pd/C gave the dipropionate **1d.**

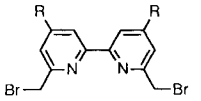
The dimethylbipyridines were functionalised by radical bromination as previously described [8] (**1a**) or by the *N*-oxide route [11] (**1a–d**). Thus, on treatment with 3-chloroperbenzoic acid (3-$ClC_6H_4CO_3H$), **1b–d** yielded mixtures of *N*-oxide **8b–d** and *N,N'*-dioxides **9b–d** from which monoalcohols **12b–d** and dialcohols **13b–d**, respectively, were obtained [12] (*via* **10b–d** and **11b–d**, resp., which were not all characterised).

The monobromides **14b**, **c** and dibromides 5**b–d** were readily available from the corresponding monoalcohols **12b**, **c** and dialcohols **13b–d** *via* mesylation followed by treatment with LiBr in THF.

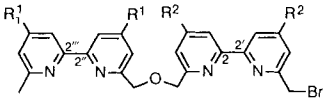
Compounds **1a** [13], **12a** [14], **13a** [14], **14a** [14], and **15a** [8] were prepared according to literature procedures and the bis[bipyridines] **16a–d** and **17a–c** by condensation of the



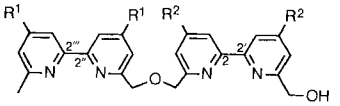
14a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$



15a R = H
b R = $CO_2(t\text{-Bu})$
c R = $CONEt_2$
d R = $CH_2CH_2CO_2(t\text{-Bu})$



16a $R^1 = R^2 = H$
b $R^1 = R^2 = CO_2(t\text{-Bu})$
c $R^1 = R^2 = CONEt_2$
d $R^1 = CH_2CH_2CO_2(t\text{-Bu})$, $R^2 = H$ (for systematic numbering, see *Exper. Part*)



17a $R^1 = R^2 = H$
b $R^1 = R^2 = CO_2(t\text{-Bu})$
c $R^1 = R^2 = CONEt_2$ (for systematic numbering, see *Exper. Part*)

appropriate functionalised bipyridines **12** and **15** (→ **16**) and substitution (→ **17**; see *Scheme*).

3.2. *Unsubstituted Oligobipyridines.* Monoalcohol **12a** (2 equiv.) and dibromide **15a** were reacted in the presence of either BuLi [2] or KO(*t*-Bu) to afford trimer **3a**. The synthesis of tetramer **4a** and pentamer **5a** followed the procedure, which has already been reported in preliminary form [3].

3.3. *Ester-Substituted Oligobipyridines.* As functional groups to be introduced on the bpy units, the *t*-Bu ester group was chosen for several reasons: *i*) an ester functionality allows a wide variety of chemical modifications to attach different substituents; *ii*) it should be stable under the basic conditions used during the formation of the ether linkages between the bipyridines; *iii*) it should increase the solubility properties of the oligobipyridines, a crucial feature for the physico-chemical studies of ion complexation and of the self-assembly process.

Various conditions were tested for the *Williamson* ether-formation step. NaH, BuLi, or LDA (lithium diisopropylamide) were not suitable. Best results were obtained using KO(*t*-Bu) in *t*-BuOH/CH_2Cl_2. Reaction of monoalcohol **12b** (2 equiv.) with dibromide **15b** (1 equiv.) gave trimer **3b** in 49% yield (reaction of **12b** with **15b** in 1:1 proportion gave the dimer monobromide **16b**, see above and *Scheme*). Condensation of **16b** with **17b** and of 2 equiv. of **17b** with **15b** gave access to tetramer **4b** and pentamer **5b**, respectively. The yields of tetramer **4b** (42%) and pentamer **5b** (21%) were low compared to the unsubstituted series (trimer **3a**, 80%; tetramer **4a**, 68%; pentamer **5a**, 72%). This may be due to side reactions of the ester function attached to the activating pyridine ring. For this reason, the syntheses were repeated with components bearing amide groups, which should be more stable than esters.

3.4. *Amide-Substituted Oligobipyridines.* Assembling of the monomer building units to dimer, trimer, tetramer, and pentamer were readily accomplished following the same

general procedure as for the esters. The yields for the critical ether-linkage step (using NaH/THF in all four cases) were now much higher than in the ester series: 72% of dimer **2c**, 76% of trimer **3c**, 56% of tetramer **4c**, and 74% of pentamer **5c**.

3.5. *Elongated Ester-Substituted Oligobipyridines.* Various observations had indicated that fully substituted oligobipyridine strands bearing bulky groups might make helicate formation sterically difficult. In addition, electron-withdrawing functions such as esters in position 4,4′ also seemed to be detrimental by decreasing the Cu^{I}-complexation ability required for helicate formation. This was found to be especially problematic in the perspective of attaching nucleoside fragments for the synthesis of the deoxyribonucleo-helicates DNH [5]. To overcome these problems, a CH_2CH_2 spacer was introduced between the bpy nucleus and the carboxylic group so as to decouple it from the bpy ligand. In addition, in the elongated series, the bulky substituents are placed farther away from the helical axis, thus diminishing steric interactions between them. Further decrease of steric interference was achieved by alternation: substituents were placed in an alternating manner on every second bipyridine unit only. In this perspective, the elongated trimer **3e** (50%) as well as the elongated-alternated trimer **3d** (61%) and pentamer **5d** (47%) were synthesised according to the *Scheme*.

4. Conclusion and Outlook. – The oligobipyridine molecules reported here represent ligand strands for the spontaneous formation of double-helical metal complexes of helicate type by complexation of metal cations of tetrahedral coordination geometry such as Cu^{I} and Ag^{I} [2–5]. The introduction of functional groups on the bpy units offers the possibility to attach a variety of substituents to the ligand backbone. Helicate formation then provides a means of arranging these groups in space in a unique double-helical fashion which may result in novel spectroscopic, electronic, photochemical, *etc.*, properties. These ligands are of interest for the study of general molecular and supramolecular features (self-organisation, cooperativity, helicity, *etc.*), for the inorganic chemistry of linear polymetallic complexes, and for the design of analogues of biological species. Numerous developments may be envisaged, and studies along these lines are under way.

We thank the *Collège de France* (*M. M. H.*), the *Fonds der Chemischen Industrie* (*Liebig* grant, *U. K.*), the *Swiss National Science Foundation* (*C. P.*), and the *CNRS-NSF* exchange programme (*J. S.*) for post-doctoral fellowships. *M. M. H.* acknowledges the University of Sydney for an *Eleanor Sophie Wood* travelling fellowship. We thank *Catherine Nguyen* for her help in the preparation of some intermediates.

Experimental Part

1. *General.* All commercially available chemicals employed were reagent grade and used without further purification, unless stated otherwise. THF and toluene were distilled over Na/benzophenone, $CHCl_3$ and CH_2Cl_2 filtered over basic aluminium oxide (act. I, *Merck*). All reactions were carried out under N_2. Magnetic stirring was used if not stated otherwise. Starting materials: 6,6′-dimethyl-2,2′-bipyridine (**1a**) was obtained from 6-bromo-2-methylpyridine [13], 6-(hydroxymethyl)-6′-methyl-2,2′-bipyridine (**12a**), 6,6′-bis(hydroxymethyl)-2,2′-bipyridine (**13a**), and 6-(bromomethyl)-6′-methyl-2,2′-bipyridine (**14a**) according to [14], and dimethyl 2,2′-bipyridine-4,4′-dicarboxylate (**6**) and 6,6′-bis(bromomethyl)-2,2′-bipyridine (**15a**) according to [8]. M.p.: *Thomas-Hoover* apparatus, model Dr. *Tottoli*; digital melting-point apparatus (*Electrotherma*); no corrections. TLC: precoated plastic sheets *Polygram Sil G/UV*$_{254}$ and *Polygram Alox N/UV*$_{254}$ (*Macherey-Nagel*). Prep. TLC: silica gel (*Merck 60 PF*$_{254}$ cotaining gypsum); aluminium oxide (Al_2O_3; *Merck 60 PF*$_{254}$, type *E*). Prep. column chromatography (CC): silica gel (*Merck 60*, 0.063–0.200 mm); aluminium oxide (Al_2O_3; *Merck*, act. II–III, 0.063–0.200 mm). Flash chromatography (FC): silica gel (*Merck 60*, 0.040–0.063 mm). UV: *Cary 219*, λ_{max} (ε). FT-IR (cm^{-1}): *Bruker IFS66*.

^{1}H-NMR: *Bruker AC 200, Bruker AM 400*; chemical shifts in ppm rel. to TMS (= 0 ppm) as internal standard. ^{13}C-NMR: broad-band decoupled. MS: FAB (positive mode) were performed at the Laboratoire de Spectrométrie de Masse, Strasbourg, and at the University of Manchester. The microanalyses were done at the Service Central de Microanalyse du CNRS, Institut de Chimie, Strasbourg.

2. *Unsubstituted Oligobipyridines* (**a** Series). *6′,6‴-Dimethyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine]* (**2a**). To a stirred soln. of **12a** (400 mg, 2.00 mmol) in THF (50 ml), NaH (96 mg, 2.20 mmol) was added. After 30 min at r.t., **14a** (526 mg, 2.00 mmol) was added and the mixture heated to reflux for 12 h. The solvent was evaporated, the residue refluxed in MeOH (50 ml) for 1 h, and the remaining solid filtered off, dissolved in a small amount of $CHCl_3$, and purified by FC (silica gel, CH_2Cl_2): 458 mg (60%) of **2a**. White solid. M.p. 188–189°. TLC (Al_2O_3, $CHCl_3$): R_f 0.50. FT-IR (KBr): 3056*w* (C=CH); 2872*w* (sat. CH); 1578*s* (C=C); 1445*s*, 1146*s* (C–O); 780*s*, 632*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.65 (*s*, 2 CH_3); 4.91 (*s*, CH_2OCH_2); 7.17 (*d*, *J* = 7.5, 2 H, H–C(5′,5‴)); 7.58 (*d*, *J* = 7.5, 2 H, H–C(5,5″)); 7.70 (*t*, *J* = 7.5, 2 H, H–C(4′,4‴)); 7.85 (*t*, *J* = 7.5, 2 H, H–C(4,4″)); 8.19 (*d*, *J* = 7.5, 2 H, H–C(3′,3‴)); 8.33 (*d*, *J* = 7.5, 2 H, H–C(3,3″)). Anal. calc. for $C_{24}H_{22}N_4O \cdot 0.5\,H_2O$ (391.46): C 73.57, H 5.87, N 14.30; found: C 73.68, H 6.02, N 14.12.

6,6″-[(2,2′-Bipyridine-6,6′-diyl)bis(methyleneoxymethylene)]-6′,6‴-dimethylbis[2,2′-bipyridine] (**3a**). To a stirred soln. of **12a** (300 mg, 1.50 mmol) in THF (100 ml) at −60° were added dropwise with a syringe 1.10 ml of 1.5M BuLi in hexane. The colour of the soln. turned from light yellow to violet at the end of the addition. The mixture was allowed to warm to r.t., treated with **15a** (175 mg, 0.50 mmol), and stirred for 18 h during which time a white precipitate formed. Then, the solvent was evaporated and the remaining solid transferred to a fritted filter funnel and washed with MeOH followed by Et_2O. The product was dissolved in $CHCl_3$ (700 ml), and after addition of MeCN (700 ml), it crystallised upon cooling to give 247 mg (80%) of **3a**. White solid. M.p. 227–229°. TLC (Al_2O_3, $CHCl_3$): R_f 0.35. FT-IR (KBr): 3059*w* (C=CH); 2872*w* (sat. CH); 1578, 1572*s* (C=C); 1438*s*, 1143*s* (C–O); 780*s*, 633*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.65 (*s*, 2 CH_3); 4.91 (*s*, 2 CH_2OCH_2); 7.17 (*d*, *J* = 7.5, 2 H, H–C(5′,5‴)); 7.58 (*d*, *J* = 7.5, 4 H, H–C(5,5″)); H–C(5^{IV},5^V)); 7.70 (*t*, *J* = 7.5, 2 H, H–C(4′,4‴)); 7.85 (*t*, *J* = 7.5, 4 H, H–C(4,4″), H–C(4^{IV},4^V)); 8.19 (*d*, *J* = 7.5, 2 H, H–C(3′,3‴)); 8.33 (*d*, *J* = 7.5, 4 H, H–C(3,3″), H–C(3^{IV},3^V)). Anal. calc. for $C_{36}H_{32}N_6O \cdot 2\,H_2O$ (616.69): C 70.05, H 5.84, N 13.62; found: C 70.44, H 5.44, N 13.45.

6′-(Bromomethyl)-6‴-methyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine] (**16a**). To a stirred soln. of **12a** (1.18 g, 5.91 mmol) in THF (75 ml), NaH dispersion (260 mg, 5.91 mmol) was added. After 1 h at r.t., **15a** (2.43 g, 7.10 mmol) was added. The soln. was refluxed for 3 h. Evaporation of the solvent and FC (silica gel, CH_2Cl_2/MeOH 99:1) afforded 1.20 g (45%) of **16a**. White solid. M.p. 142–144°. TLC (Al_2O_3, CH_2Cl_2): R_f 0.80. IR (KBr): 3060*w* (C=CH); 2870*w* (sat. CH); 1580*s*–1560*s* (C=C); 1430*s*; 1140*s*; 770*s*; 630*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.65 (*s*, CH_3–C(6‴)); 4.63 (*s*, CH_2Br); 4.91 (*s*, CH_2OCH_2); 7.17 (*d*,*J* = 7.5, 1 H); 7.47 (*d*, *J* = 7.5, 1 H); 7.58 (*d*, *J* = 7.5, 2 H); 7.70 (*t*, *J* = 7.5, 1 H); 7.80 (*t*, *J* = 7.5, 1 H); 7.87 (*t*, *J* = 7.5, 2 H); 8.19 (*d*, 1 H); 8.30–8.36 (*m*, 3 H). Anal. calc. for $C_{24}H_{21}BrN_4O \cdot H_2O$ (479.30): C 60.12, H 4.83, N 11.68; found: C 60.70, H 4.46, N 11.13.

6′-(Hydroxymethyl)-6‴-methyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine][7]) (**17a**). A stirred soln. of **16a** (500 mg, 1.08 mmol) in DMF (50 ml) was treated with NaOAc (850 mg, 10.4 mmol) at 130° for 10 h. The soln. was concentrated *in vacuo*, H_2O was added, and the precipitated bipyridine methyl acetate (429 mg) separated by filtration. The acetate was dissolved in MeOH (50 ml), a soln. of NaOH (200 mg, 5.00 mmol) in H_2O (1.5 ml) added, and the mixture refluxed for 30 min. Upon cooling to r.t., the product crystallised. Filtration and recrystallisation from EtOH gave 264 mg (62%) of **17a**. White solid. M.p. 178° (EtOH). TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.40 ^{1}H-NMR (200 MHz, $CDCl_3$): 2.65 (*s*, CH_3–C(6‴)); 4.83 (*s*, CH_2OH); 4.91 (*s*, CH_2OCH_2); 7.17 (*d*, *J* = 7.5, 1 H); 7.27 (*d*, *J* = 7.5, 1 H); 7.58 (*d*, *J* = 7.5, 1 H); 7.61 (*d*, *J* = 7.5, 1 H); 7.72 (*t*, *J* = 7.5, 1 H); 7.86–7.92 (*m*, 3 H); 8.20 (*d*, *J* = 7.5, 1 H); 8.24–8.28 (*m*, 3 H). Anal. calc. for $C_{24}H_{22}N_4O_2$ (398.45): C 72.34, H 5.56; found: C 71.82, H 5.47.

6′,6‴-Dimethyl-6,6″-{[oxybis(methylene)]bis(2,2′-bipyridine-6′,6-diyl)bis(methyleneoxymethylene)}bis[2,2′-bipyridine] (**4a**). To a stirred soln. of **17a** (100 mg, 0.25 mmol) in THF (30 ml) and DMSO (0.5 ml), KO(*t*-Bu) (36.5 mg, 0.32 mmol) was added. After 30 min at r.t., **16a** (116 mg, 0.25 mmol) was added and the mixture refluxed for 1 h. It was cooled to r.t., and after 48 h, a precipitate had formed which was filtered off, washed with H_2O and Et_2O, and dried thoroughly: 134 mg (68%) of **4a**. M.p. > 260°. ^{1}H-NMR (400 MHz, CF_3COOD/(D_6)acetone 1:9): 3.12 (*s*, 2 CH_3); 5.19, 5.36, 5.38 (3*s*, 3 CH_2OCH_2); 8.23–8.89 (*m*, 24 H). FAB-MS (pos. mode): 779.2 ($[M + H]^+$, $C_{48}H_{43}N_8O_3$, calc. 778.9). Anal. calc. for $C_{48}H_{42}N_8O_3$ (778.9): C 74.01, H 5.43; found: C 73.20, H 5.26.

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[7]) Systematic name of **17a**: 6‴-Methyl-6′,6″-[oxybis(methylene)]bis[2,2′-bipyridine]-6-methanol.

6,6''-[(2,2'-Bipyridine-6,6'-diyl)bis(methyleneoxymethylene)bis(2,2'-bipyridine-6',6-diyl)bis(methyleneoxymethylene)]-6',6'''-dimethylbis[2,2'-bipyridine] (**5a**). To a stirred soln. of **17a** (200 mg, 0.50 mmol) in THF (30 ml) and DMSO (0.5 ml), KO(*t*-Bu) (70 mg, 0.62 mmol) was added. After 30 min at r.t., **15a** (116 mg, 0.25 mmol) was added and the mixture refluxed for 15 h, during which time a precipitate formed. After addition of MeOH (1.0 ml), the precipitate was filtered off, washed with MeOH/H_2O 1:1 and Et_2O, and dried: 175 mg (72%) of **5a**. M.p. > 260°. ^{1}H-NMR (400 MHz, CF_3COOD/(D_6)acetone 1:9): 3.12 (*s*, 2 CH_3); 5.19, 5.36, 5.38 (3*s*, 4 CH_2OCH_2); 8.23–8.89 (*m*, 30 H). FAB-MS (pos. mode): 977.0 ($[M + H]^+$, calc. 977.1). Anal. calc. for $C_{60}H_{52}N_{10}O_4 \cdot 3H_2O$ (1031.14): C 69.88, H 5.67, N 13.58; found: C 69.74, H 5.20, N 12.97.

3. *Ester-Substituted Oligobipyridines* (**b** Series). *Di(*tert*-butyl) 6,6'-Dimethyl-2,2'-bipyridine-4,4'-dicarboxylate* (**1b**). A soln. of LiO(*t*-Bu) in *t*-BuOH prepared from 1.5M BuLi in hexane (40 ml) and *t*-BuOH (150 ml) was added dropwise to a stirred soln. of **6** (4.00 g, 1.33 mmol) in toluene (500 ml) at 80°. After the addition, the soln. was stirred for 30 min at 80°, then cooled to r.t., washed with H_2O (3 × 150 ml), dried ($MgSO_4$), and evaporated and the residue crystallised from $CHCl_3$/MeOH: 4.60 g (90%) of **1b**. White needles. M.p. 193° ($CHCl_3$/MeOH): TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.7 IR (KBr): 3094*w* (C=C); 2999, 2975*m* (sat. CH); 1715*s* (C=O); 1572*m* (C=C); 1392, 1367*m* (*t*-Bu); 1297*s*, 1220*s*, 1164*s*, 1136*s*, 935*m*, 848*m*, 769*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.60 (*s*, 2 *t*-Bu); 2.68 (*s*, 6 H, CH_3–C(6,6')); 7.65 (*s*, 2 H, H–C(5,5')); 8.62 (*s*, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.62 (CH_3–C(6,6')); 28.11 ((CH_3)C); 82.25 ((CH_3)$_3C$); 117.72 (C(5,5')); 122.50 (C(3,3')); 140.57, 156.30, 159.01 (C(2,2'), C(4,4'), C(6,6')); 164.65 (C=O). Anal. calc. for $C_{22}H_{28}N_2O_4$ (384.46): C 68.72, H 7.34, N 7.29; found: C 68.33, H 7.41, N 7.24.

*4,4'-Bis[(*tert*-butoxy)carbonyl]-6,6'-dimethyl-2,2'-bipyridine 1-Oxide* (**8b**) *and 4,4'-Bis[(*tert*-butoxy)carbonyl]-6,6'-dimethyl-2,2'-bipyridine 1,1'-Dioxide* (**9b**). A soln. of 3-$ClC_6H_4CO_3H$ (3.85 g, 18.8 mmol) in $CHCl_3$ (100 ml) was added dropwise to a stirred soln. of **1b** (6.00 g, 15.6 mmol) in $CHCl_3$ (250 ml) maintaining the temp. at 0–5°. The soln. was allowed to warm to r.t., stirred for 4 h, washed with sat. aq. Na_2CO_3 soln. (2 × 100 ml) and sat. aq. NaCl soln. (2 × 100 ml), dried ($MgSO_4$), and evaporated. The residue was separated by FC (silica gel, $CHCl_3$, then $CHCl_3$/MeOH 95:5): 5.10 g (81%) of **8b** and 1.17 g (18%) of **9b**, both white solids.

Data of **8b**: M.p. 160–161° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.5. FT-IR (KBr): 3129*w* (C=CH); 3000, 2972, 2933*m* (sat. CH); 1716*s* (C=O); 1597, 1572*m* (C=C); 1396, 1367*m* (*t*-Bu); 1280*s*, 1170*s*, 1142*s*, 847*m*, 773*m*, 752*m*, 667*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.59 (*s*, 2 *t*-Bu); 2.57 (*s*, CH_3–C(6)); 2.67 (*s*, CH_3–C(6')); 7.71, 7.81 (2*s*, H–C(5), H–C(5')); 8.37 (*s*, H–C(3')); 8.75 (*s*, H–C(3)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.33 (CH_3–C(6)); 24.50 (CH_3–C(6')); 28.05 ((CH_3)$_3$C); 82.37 ((CH_3)$_3C$); 121.55, 123.06, 125.46, 125.66 (C(3,3'), C(5,5')); 127.16, 140.01, 147.27, 149.91, 150.38, 159.13 (C(2,2'), C(4,4'), C(6,6')); 163.08, 164.18 (C=O). Anal. calc. for $C_{22}H_{28}N_2O_5$ (400.46): C 65.98, H 7.05, N 7.00; found: C 65.77, H 7.13, N 7.08.

Data of **9b**: M.p. 195–196° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.2. FT-IR (KBr): 3094*w* (C=C); 2999, 2975*m* (sat. CH); 1715*s* (C=O); 1572*m* (C=C); 1392, 1367*m* (*t*-Bu); 1297*s*, 1220*s*, 1164*s*, 1136*s*, 936*m*, 848*m*, 769*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.50 (*s*, 2 *t*-Bu); 2.51 (*s*, 6 H, CH_3–C(6,6')); 7.68 (*s*, 2 H, H–C(5,5')); 7.87 (*s*, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.62 (CH_3–C(6,6')); 28.11 ((CH_3)$_3$C); 82.25 ((CH_3)$_3C$); 117.72 (C(5,5')); 122.50 (C(3,3')); 140.57, 156.30, 159.01 (C(2,2'), C(4,4'), C(6,6')); 164.65 (C=O). Anal. calc. for $C_{22}H_{28}N_2O_6$ (416.46): C 63.44, H 6.78, N 6.73; found: C 63.36, H 6.70, N 6.66.

*Di(*tert*-butyl) 6-(Hydroxymethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxylate* (**12b**). A mixture of **8b** (0.74 g, 1.85 mmol) and $(CF_3CO)_2O$ (10 ml) was stirred at r.t. for 1 h. The excess anhydride was evaporated and the formed trifluoroacetate **10b** thoroughly dried under vacuum. To a soln. of the crude **10b** in THF/H_2O 2:1 (200 ml), Na_2CO_3 (0.15 g, 1.4 mmol) was added and stirred overnight. The THF was evaporated, the product extracted into $CHCl_3$, the org. layer dried ($MgSO_4$) and evaporated, and the residue crystallised from $CHCl_3$/hexane: **12b** (0.68 g, 91%). Cream needles. M.p. 205–206° ($CHCl_3$/hexane). TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.20. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.56 (*s*, 2 *t*-Bu); 2.70 (*s*, CH_3–C(6')); 3.73 (*t*, *J* = 5.5, OH); 4.88 (*d*, *J* = 4.8, CH_2–C(6)); 7.68, 7.75 (2*s*, H–C(5), H–C(5')); 8.63 (*s*, H–C(3')); 8.79 (*s*, H–C(3)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.56 (CH_3–C(6')); 28.08 ((CH_3)$_3$C); 64.23 (CH_2OH); 82.63 ((CH_3)$_3C$); 117.55, 119.40, 119.80, 122.87 (C(3,3'), C(5,5')); 141.16, 142.34, 155.10, 155.34, 159.18, 159.56 (C(2,2'), C(4,4'), C(6,6')); 164.05, 164.45 (C=O). Anal. calc. for $C_{22}H_{28}N_2O_5$ (400.46): C 65.98, H 7.05, N 7.00; found: C 65.87, H 6.97, N 7.00.

*Di(*tert*-butyl) 6,6'-Bis(hydroxymethyl)-2,2'-bipyridine-4,4'-dicarboxylate* (**13b**). A mixture of **9b** (3.08 g, 7.40 mmol) and $(CF_3CO)_2O$ (25 ml) was stirred at r.t. for 1 h, the excess anhydride evaporated, and the yellow, solid bis(trifluoroacetate) **11b** dissolved in THF (20 ml) and treated with sat. aq. $NaHCO_3$ soln. (30 ml) at r.t. for 1 h. The THF was evaporated and the product extracted with $CHCl_3$ (2 × 100 ml). The combined org. layers were dried ($MgSO_4$) and evaporated and the residue crystallised from $CHCl_3$/hexane: 1.95 g (63%) of **13b**. White solid. M.p. 183–184° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$/MeOH 95:5): R_f 0.20. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.62 (*s*, 2 *t*-Bu); 3.66 (*t*, *J* = 5.1, 2 OH); 4.90 (*d*, *J* = 5.0, 2 CH_2O); 7.78 (*s*, 2 H, H–C(5,5')); 8.77 (*s*, 2 H, H–C(3,3')).

^{13}C-NMR (50.3 MHz, $CDCl_3$): 28.06 ($(CH_3)_3C$); 64.27 (CH_2OH); 82.84 ($(CH_3)_3C$); 119.27, 120.20, 119.80, 141.23, 154.80, 159.85 (C of bpy); 163.96 (C=O). Anal. calc. for $C_{22}H_{28}N_2O_6$ (416.46): C 63.44, H 6.78, N 6.73; found: C 63.60, H 6.75, N 6.69.

*Di(*tert*-butyl) 6-(Bromomethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxylate* (**14b**). A stirred soln. of **12b** (0.62 g, 1.55 mmol) in CH_2Cl_2 (100 ml) at 0° was treated successively with MsCl (0.48 ml, 6.19 mmol) and Et_3N (1.73 ml, 12.4 mmol). The resulting yellow soln. was allowed to warm to r.t. and stirred for 20 min. The mixture was washed twice with sat. aq. NH_4Cl soln. (100 ml) and dried ($MgSO_4$). Evaporation of the solvent gave the crude mesylate as a brown oil which was dissolved in THF (100 ml). To the stirred soln., anh. LiBr (3.00 g, 34.5 mmol) was added and the mixture heated to 50° for 30 min. After evaporation, the crude product was partitioned between $CHCl_3$/sat. NH_4Cl soln. 1:1 (200 ml), the aq. layer separated and extracted with $CHCl_3$ (100 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the residue purified by CC (Al_2O_3, $CHCl_3$): 0.53 g (74%) of **14b**. White needles. M.p. 178–179° ($CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$): R_f 0.90. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.63 (*s*, 2 *t*-Bu); 2.68 (*s*, CH_3–C(6')); 4.67 (*s*, CH_2Br); 7.67, 7.93 (2*s*, 2 H, H–C(5,5)); 8.67, 8.78 (2*s*, 2 H, H–C(3',3)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.53 (CH_3–C(6')); 28.04 ($(CH_3)_3C$); 33.50 (CH_2Br); 82.34, 82.66 ($(CH_3)_3C$); 117.85, 119.86, 122.71, 122.83, 140.59, 141.48, 155.38, 156.56, 157.22, 159.02 (C of bpy); 163.85, 164.47 (C=O). Anal. calc. for $C_{22}H_{27}N_2O_4$ (463.36): C 57.02, H 5.87, N 6.05; found: C 56.86, H 5.80, N 5.99.

*Di(*tert*-butyl) 6,6'-Bis(bromomethyl)-2,2'-bipyridine-4,4'-dicarboxylate* (**15b**). A stirred suspension of **13b** (2.31 g, 5.54 mmol) in CH_2Cl_2 (150 ml) at 0° was treated successively with MsCl (2.14 ml, 27.6 mmol) and Et_3N (6.20 ml, 44.8 mmol). The resulting yellow soln. was allowed to warm to r.t. and stirred for 15 min. The mixture was washed with sat. aq. NH_4Cl soln. (2 × 100 ml), dried ($MgSO_4$), and evaporated. To the crude dimesylate (brown oil) in THF (150 ml), anh. LiBr (6.01 g, 70.2 mmol) was added under stirring and the mixture heated to 40° for 1 h. After evaporation, the crude product was partitioned between $CHCl_3$/sat. aq. NH_4Cl soln. 1:1 (200 ml). The aq. layer was separated and extracted with $CHCl_3$ (100 ml). The combined org. layer was dried ($MgSO_4$) and evaporated and the residue purified by CC (Al_2O_3, CH_2Cl_2): 2.41 g (71%) of **15b**. White needles. M.p. 183–184° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.75. FT-IR (KBr): 3069*w* (C=CH); 2975*m* (sat. CH); 1712*s* (C=O); 1593*w*, 1561*m* (C=C); 1367*m* (*t*-Bu); 1297*s*, 1153*s* (C–O); 946*m*, 918*m*, 844*m*, 769*m*, 689*m*, 590*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.63 (*s*, 2 *t*-Bu); 4.67 (*s*, CH_2Br); 7.95 (*s*, 2 H, H–C(5,5)); 8.81 (*s*, 2 H, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 28.11 ($(CH_3)_3C$); 46.51 (CH_2Br); 82.89 ($(CH_3)_3C$); 120.15, 123.15, 141.69, 155.86, 157.37 (C of bpy); 163.84 (C=O). Anal. calc. for $C_{22}H_{26}Br_2N_2O_4$ (542.25): C 48.73, H 4.83, N 5.17; found: C 48.95, H 4.83, N 5.19.

*Tetra(*tert*-butyl) 6',6'''-Dimethyl-6,6''-[oxybis(methylene)]bis[2,2'-bipyridine]-4,4',4'',4'''-tetracarboxylate* (**2b**). To a stirred soln. of **12b** (120 mg, 0.30 mmol) in *t*-BuOH (60 ml), KO(*t*-Bu) (40 mg, 0.36 mmol) was added. After 1 h, **14b** (140 mg, 0.30 mmol) in CH_2Cl_2 (5 ml) was added and the soln. stirred at r.t. for 2 h. A second portion of base was added (10 mg, 0.09 mmol) and the soln. refluxed overnight. Evaporation afforded a yellow solid which was purified by CC (Al_2O_3, CH_2Cl_2): 100 mg (43%) of **2b**. White solid. M.p. 182–183° ($CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$): R_f 0.85. FT-IR (KBr): 3090*w* (C=CH); 2980, 2928*m* (sat. CH); 1719*s* (C=O); 1593*w*, 1564*m* (C=C); 1392, 1367*m* (*t*-Bu); 1297*s*, 1164*s* (C–O); 1132*s*, 942*m*, 844*m*, 769*m*, 692*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.52, 1.53 (2*s*, 4 *t*-Bu); 2.50 (*s*, 6 H, CH_3–C(6',6''')); 4.82 (*s*, CH_2OCH_2); 7.79 (*s*, 2 H, H–C(5',5''')); 8.46 (*s*, 2 H–C(5,5'')); 9.38, 9.53 (2*s*, 2 H–C(3,3''), 2 H–C(3',3''')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.59 (CH_3–C(6,6''')); 28.10 ($(CH_3)_3C$); 73.90 (CH_2OCH_2); 82.63, 82.40 ($(CH_3)_3C$); 117.77, 119.48, 120.61, 122.68, 140.62, 141.22, 155.91, 156.24, 158.98, 159.05 (C of bpy); 164.41, 164.58 (C=O). FAB-MS (pos. mode): 783.2 (calc. 782.9). Anal. calc. for $C_{44}H_{54}N_4O_9$ (782.90): C 67.50, H 6.95, N 7.16; found: C 67.35, H 6.82, N 7.05.

*Tetra(*tert*-butyl) 6'-(Bromomethyl)-6'''-methyl-6,6''-[oxybis(methylene)]bis[2,2'-bipyridine]-4,4',4'',4'''-tetracarboxylate* (**16b**). To a stirred soln. of **12b** (290 mg, 0.724 mmol) in *t*-BuOH (50 ml) was added KO(*t*-Bu) (90 mg, 0.80 mmol). After 1 h at r.t., **15b** (0.40 g, 0.737 mmol) in CH_2Cl_2 (5 ml) was added. The soln. was stirred at r.t. for 1 h and refluxed for 1 h. Addition of H_2O (1.0 ml) and evaporation afforded a yellow solid which was purified by CC (silica gel, CH_2Cl_2/MeOH 95:5). Crystallisation from $CHCl_3$/MeOH gave 190 mg (30%) of **16b**. White solid. M.p. 113° (Et_2O, hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.75. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.58, 1.59, 1.60, 1.61 (4*s*, *t*-Bu); 2.68 (*s*, CH_3–C(6''')); 4.67 (*s*, CH_2Br); 4.97 (*s*, CH_2OCH_2); 7.24 (*s*, 1 H); 7.65 (*d*, J = 1.4, 1 H); 7.93 (*d*, J = 1.5, 1 H); 8.63 (*s*, 1 H); 8.81 (*s*, 1 H); 8.77 (*s*, 2 H); 8.81 (*s*, 1 H). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.54 (CH_3–C(6''')); 28.06 ($(CH_3)_3C$); 33.45 (CH_2Br); 73.80, 73.88 (CH_2O); 82.26, 82.37, 82.49, 82.69 ($(CH_3)_3C$); 117.75, 119.45, 119.62, 119.91, 120.60, 120.98, 122.66, 122.80, 140.65, 141.20, 141.28, 141.57, 155.43, 155.84, 156.18, 157.28, 159.01, 159.90 (C of bpy); 163.81, 164.30, 164.36, 164.50 (C=O). Anal. calc. for $C_{44}H_{53}BrN_4O_{10} \cdot 3H_2O$ (915.86): C 57.69, H 6.49; found: C 57.60, H 6.19.

*Tetra(*tert*-butyl) 6'-(Hydroxymethyl)-6'''-methyl-6,6''-[oxybis(methylene)]bis[2,2'-bipyridine]-4,4',4'',4'''-tetracarboxylate* (**17b**). A stirred soln. of **16b** (270 mg, 0.31 mmol) in DMF (10 ml) was treated with NaOAc

(200 mg, 2.4 mmol) at 50° for 1 h. The DMF was evaporated and the residue dissolved in CH_2Cl_2/H_2O. The org. layer was separated and the aq. phase extracted twice with CH_2Cl_2. The combined org. layer was dried ($MgSO_4$) and evaporated and the crude corresponding acetate (240 mg) in THF (35 ml) treated with a Na_2CO_3 soln. (60 mg, 0.57 mmol) in H_2O (30 ml), heated to reflux overnight, and cooled to r.t. The THF was evaporated, the product extracted into CH_2Cl_2 and dried ($MgSO_4$), and the residue purified by CC (silica gel, CH_2Cl_2/MeOH 95:5): 200 mg (81%) of **17b**. White solid. M.p. 113° (Et_2O/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.30. FT-IR (KBr): 3508*m* (br. OH); 2978*m*, 2928*w* (sat. CH); 1719*s* (C=O); 1596*w*, 1568*m* (C=C); 1392, 1367*m* (*t*-Bu); 1301*s*, 1160*s* (C–O); 1135*m*, 848*m*, 769*m*, 756*m*, 692*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.60, 1.61, 1.62 (3*s*, 4 *t*-Bu); 2.71 (*s*, CH_3–C(6‴)); 4.91 (*s*, CH_2OH); 5.00 (*s*, CH_2OCH_2); 7.67 (*d*, *J* = 1.1, H–C(5‴)); 7.78 (*d*, *J* = 1.0, H–C(5′)); 8.08, 8.10 (2*d*, *J* = 1.2, H–C(5), H–C(5″)); 8.64 (*s*, H–C(3‴)); 8.78–8.80 (*m*, H–C(3), H–C(3′), H–C(3″)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.56 (CH_3–C(6‴)); 28.06 ((CH_3)$_3$C); 64.20 (CH_2OH); 73.77, 73.88 (CH_2O); 82.31, 82.43, 82.60, 82.69 ((CH_3)$_3C$); 117.77, 119.28, 119.50, 120.00, 120.60, 121.01, 122.71, 140.59, 141.23, 155.28, 155.84, 156.18, 158.90, 159.04, 159.16 (C of bpy); 164.04, 164.21, 164.53 (C=O). Anal. calc. for $C_{44}H_{54}N_4O_{10}$ (798.90): C 66.15, H 6.81, N 7.01; found: C 65.82, H 6.87, N 6.71.

*Tetra(*tert*-butyl) 6,6″-{{4,4′-Bis[(*tert*-butoxy)carbonyl]-2,2′-bipyridine-6,6′-diyl}bis(methyleneoxymethylene)}-6′,6‴-dimethylbis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxylate* (**3b**). To a stirred soln. of **12b** (1.00 g, 2.50 mmol) in *t*-BuOH (250 ml), KO(*t*-Bu) (0.34 g, 3.00 mmol) was added. After 1.25 h at r.t., **15b** (0.66 g, 1.22 mmol) CH_2Cl_2 (10 ml) was added dropwise. The soln. was refluxed for 4 h, a second portion of base added (0.10 g, 0.89 mmol), and the soln. refluxed overnight. Evaporation afforded a yellow solid which was purified by CC (Al_2O_3, $CHCl_3$). Crystallisation from $CHCl_3$/MeOH gave 0.70 g (49%) of **3b**. White solid. M.p. 135–136° ($CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$): R_f 0.80. FT-IR (KBr): 3090*w* (C=CH); 2978*m*, 2928*w* (sat. CH); 1723*s* (C=O); 1593*w*, 1564*m* (C=C); 1392, 1367*m* (*t*-Bu); 1297*s*, 1164*s* (C–O); 1132*s*, 942*m*, 844*m*, 769*m*, 756*m*, 692*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.55, 1.59, 1.61 (3*s*, 6 *t*-Bu); 2.68 (*s*, 6 H, CH_3–C(6′,6‴)); 4.98 (*s*, 2 CH_2OCH_2); 7.66 (*s*, 2 H, H–C(5′,5‴)); 8.06 (*s*, 4 H, H–C(5,5″), H–C(5^{IV},5^{V})); 8.63, 8.78 (2*s*, 6 H, H–C(3,3″), H–C(3′,3‴), H–C(3^{IV},3^{V})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.57 (CH_3–C(6′,6‴)); 28.05 ((CH_3)$_3$C); 73.83 (CH_2O); 82.27, 82.39 ((CH_3)$_3C$); 117.73, 119.44, 120.58, 122.66, 140.50, 141.18, 155.82, 156.19, 158.99 (C of bpy); 164.36 (C=O). FAB-MS (pos. mode): 1181.5 (calc. 1181.4). Anal. calc. for $C_{66}H_{80}N_6O_{14}$ (1181.35): C 67.10, H 6.83, N 7.11; found: C 67.24, H 6.89, N 6.56.

*Tetra(*tert*-butyl) 6′,6‴-Dimethyl-6,6″-{[oxybis(methylene)]bis{4,4′-bis[(*tert*-butoxy)carbonyl]-2,2′-bipyridine-6′,6-diyl}bis(methyleneoxymethylene)}bis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxylate* (**4b**). To a stirred soln. of **17b** (100 mg, 0.125 mmol) in *t*-BuOH (25 ml) was added KO(*t*-Bu) (15 mg, 0.137 mmol). After 1.5 h at r.t., **16b** (108 mg, 0.125 mmol) in CH_2Cl_2 (2 ml) was added dropwise. The soln. was stirred at 60° for additional 15 h. After addition of H_2O (1.0 ml) the solvent was evaporated. Purification was effected by prep. TLC (Al_2O_3, hexane/CH_2Cl_2 1:1): 82 mg (42%) of **4b**. White solid. M.p. 137–139° ($CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$): R_f 0.70. FT-IR (KBr): 3090*w* (C=CH); 2975*m*, 2928*w* (sat. CH); 1722*s* (C=O); 1594*w*, 1563*m* (C=C); 1390, 1365*m* (*t*-Bu); 1295*s*, 1162*s* (C–O); 1130*s*, 767*m*, 754*m*, 690*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.55, 1.59, 1.61 (3*s*, 8 *t*-Bu); 2.68 (*s*, CH_3–C(6′,6‴)); 4.98 (*s*, 3 CH_2OCH_2); 7.66 (2*s*, 2 H, H–C(5′,5‴)); 8.06 (*s*, 6 H, H–C(5,5″), H–C(5^{IV},5^{VI}), 2 H–C(5^{V},5^{VII})); 8.63, 8.78 (2*s*, 8 H, H–C(3,3″), 2 H–C(3′,3‴), 2 H–C(3^{IV}, 3^{VI}), 2 H–C(3^{V}, 3^{VII})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.57 (CH_3–C(6′,6‴)); 28.05 ((CH_3)$_3$C); 73.83 (CH_2OCH_2); 82.27, 82.39 ((CH_3)$_3C$); 117.73, 119.44, 120.58, 122.66, 140.50, 141.18, 155.82, 156.21, 158.99 (C of bpy); 164.36 (C=O). FAB-MS (pos. mode): 1581.0 (calc. 1579.8). Anal. calc. for $C_{88}H_{106}N_8O_{19}$ (1579.79): C 66.90, H 6.76; found: C 67.04, H 7.16.

*Tetra(*tert*-butyl) 6,6″-{{4,4′-Bis[(*tert*-butoxy)carbonyl]-2,2′-bipyridine-6,6′-diyl}bis(methyleneoxymethylene)bis{4,4′-bis[(*tert*-butoxy)carbonyl]-2,2′-bipyridine-6′,6-diyl}bis(methyleneoxymethlene)}-6′,6‴-dimethylbis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxylate* (**5b**). To a stirred soln. of **17b** (125 mg, 0.15 mmol) in *t*-BuOH (25 ml), KO(*t*-Bu) (20 mg, 0.18 mmol) was added. After 1.5 h at r.t, **15b** (44 mg, 0.074 mmol) in CH_2Cl_2 (2 ml) was added dropwise. The soln. became turbid and was stirred for additional 10 h. After addition of H_2O (1.0 ml) and evaporation, the residue was purified by prep. TLC (Al_2O_3, hexane/CH_2Cl_2 1:1): 32 mg (21%) of **5b**. White solid. M.p. 135–136° ($CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$): R_f 0.80. FT-IR (KBr): 3090*w* (C=CH); 2978*m*, 2928*w* (sat. CH); 1723*s* (C=O); 1593*w*, 1564*m* (C=C); 1392, 1367*m* (*t*-Bu); 1297*s*, 1164*s* (C–O); 1132*s*, 942*m*, 844*m*, 769*m*, 756*m*, 692*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.55, 1.59, 1.61 (3*s*, 10 *t*-Bu); 2.68 (*s*, 6 H, CH_3–C(6′,6‴)); 4.98 (*s*, 4 CH_2OCH_2); 7.66 (*s*, 2 H, H–C(5′,5‴)); 8.06 (*s*, 8 H, H–C(5,5″), H–C(5^{IV},5^{VI}), H–C(5^{V},5^{VII}), H–C(5^{VIII},5^{IX})); 8.63, 8.78 (2*s*, 10 H, H–C(3,3″), H–C(3′,3‴); H–C(3^{IV},3^{VI}), H–C(3^{V},3^{VII}), H–C(3^{VIII},3^{IX})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.57 (CH_3–C(6′,6‴)); 28.05 ((CH_3)$_3$C); 73.83 (CH_2OCH_2); 82.27, 82.39 ((CH_3)$_3C$); 117.73, 119.44, 120.58, 122.66, 140.50, 141.18, 155.82, 156.22, 158.99 (C of bpy); 164.36 (C=O). FAB-MS (pos. mode): 1979.5 (calc. 1979.24). Anal. calc. for $C_{110}H_{132}N_{10}O_{24}$ (1978.24): C 66.78, H 6.73, N 7.08; found: C 66.74, H 7.07, N 6.41.

4. *Amide-Substituted Oligo(bipyridines)* (**c** Series). *N,N,N',N'-Tetraethyl-6,6'-dimethyl-2,2'-bipyridine-4,4'-dicarboxamide* (**1c**). To a stirred suspension of $AlCl_3$ (16.0 g, 118 mmol) in toluene (250 ml), Et_2NH (21.0 ml, 197 mmol) was added dropwise, while the temp. was kept at 25–30° (ice-bath). Then, **6** (5.90 g, 19.6 mmol) was added. The mixture was stirred at 40° for 3 h (TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): no **6** left), H_2O (100 ml) added dropwise, the org. layer separated and evaporated, and the crude product filtered over Al_2O_3 (CH_2Cl_2/MeOH 98:2) and crystallised from acetone: 7.20 g (96%) of **1c**. White solid. M.p. 191–192° (acetone). TLC (Al_2Cl_3, $CHCl_3$/MeOH 98:2): R_f 0.40. IR (KBr): 3060*w* (C=CH); 2960, 2920*m* (sat. CH); 1625*s* (C=O); 1590, 1550*m* (C=C); 1470*s*, 1380*m*, 890*s*, 835*s*, 710*m*, 690*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.14 (*t*, J = 7, 2 CH_3CH_2); 1.28 (*t*, J = 7, 2 CH_3CH_2); 2.64 (*s*, 6 H, CH_3–C(6,6')); 3.25 (*q*, J = 7, 2 CH_3CH_2); 3.57 (*q*, J = 7, 2 CH_3CH_2); 7.14 (*d*, J = 1.1, 2 H, H–C(5,5')); 8.20 (*d*, J = 1.1, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.81, 14.16 (CH_3CH_2); 24.59 (CH_3–C(6,6')); 39.20, 43.17 (CH_3CH_2); 115.23 (C(5,5')); 122.22 (C(3,3')); 145.79 (C(4,4')); 155.47 (C(2,2')); 158.55 (C(6,6')); 169.09 (C=O). EI-MS (70 eV): 382.49 (M^+). Anal. calc. for $C_{22}H_{30}N_4O_2$ (382.49): C 69.08, H 7.91, N 14.60; found: C 69.33, H 8.37, N 14.44.

4,4'-Bis(diethylcarbamoyl)-6,6'-dimethyl-2,2'-bipyridine 1-Oxide (**8c**) *and 4,4'-Bis(diethylcarbamoyl)-6,6'-dimethyl-2,2'-bipyridine 1,1'-Dioxide* (**9c**). A soln. of 3-$ClC_6H_4CO_3H$ (4.8 g, 27.9 mmol) in $CHCl_3$ (100 ml) was added dropwise to a stirred soln. of **1c** (5.80 g, 15.2 mmol) in $CHCl_3$ (100 ml) keeping the temp. at 0–5°. The soln. was allowed to warm to r.t., stirred for 2 h, then washed subsequently with sat. aq. Na_2CO_3 soln. (20 ml) and H_2O (2 × 20 ml), dried ($MgsO_4$), and evaporated. FC (silica gel, CH_2Cl_2/MeOH first 96:4 then 90:10) gave 1.80 g (30%) of **8c** and 3.10 g (49%) of **9c**, both white solids.

Data of **8c**. M.p. 159–161° (acetone/Et_2O). TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): R_f 0.55. IR (KBr): 3060*w* (C=CH); 2960s, 2880*m* (sat. CH); 1620*s* (C=O); 1550*s* (C=C); 1430*s*, 1270*s* (NO); 820*m*, 755*m*, 700*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.15–1.38 (*m*, 4 CH_3CH_2); 2.59 (*s*, CH_3–C(6)); 2.64 (*s*, CH_3–C(6')); 3.22–3.40 (*m*, 2 CH_3CH_2); 3.45–3.53 (*m*, 2 CH_3CH_2); 7.21 (*d*, J = 1.1, H–C(5')); 7.36 (*d*, J = 2.4, H–C(5)); 8.10 (*d*, J = 2.5, H–C(3)); 8.88 (*d*, J = 1.1, H–C(3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.81, 14.15 (CH_3CH_2); 18.38 (CH_3–C(6)); 24.59 (CH_3–C(6')); 39.31, 43.31 (CH_3CH_2); 119.33, 120.95, 123.57, 123.98 (C(3), C(5), C(3'), C(5')); 145.20, 146.51 (C(4), C(4')); 149.08, 150.09, 158.75 (C(2), C(6), C(2'), (C(6')); 168.10, 168.66 (C=O). EI-MS (70 eV): 399 (MH^+). Anal. calc. for $C_{22}H_{30}N_4O_3$ (398.51): C 69.08, H 7.91, N 14.60; found: C 68.05, H 7.96, N 14.48.

Data of **9c**. M.p. 152–155° (CH_2Cl_2). TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): R_f 0.40. IR (KBr): 3060*w* (C=CH); 2960*m*, 2920*w* (sat. CH); 1625*s* (C=O); 1540*s* (C=C); 1420*m*, 1375*m*, 1260*s* (NO); 800*m*, 760*w*, 720*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.13–1.38 (*m*, 4 CH_3CH_2); 2.59 (*s*, CH_3–C(6,6')); 3.38–3.54 (*m*, 4 CH_3CH_2); 7.41, 7.45 (2*d*, J = 2.3, 4 H). EI-MS (70 eV): 415 (MH^+). Anal. calc. for $C_{22}H_{30}N_4O_4$ (414.51): C 69.08, H 7.91, N 14.60; found: C 68.05, H 7.96, N 14.48.

N,N,N',N'-Tetraethyl-6-(hydroxymethyl)-6'-methyl-2,2'-bipyridine-4,4'-dicarboxamide (**12c**). At r.t., **8c** (1.50 g, 3.76 mmol) was treated with $(CF_3CO)_2O$ (15 ml) for 30 min. The excess anhydride was evaporated and the product dried under vacuum thoroughly. To the formed crude trifluoroacetate **10c** in THF/H_2O 1:1 (60 ml), Na_2CO_3 (5.00 g, 47.2 mmol) was added, the soln. stirred overnight, the THF evaporated, the product extracted into CH_2Cl_2, the org. layer dried ($MgSO_4$) and evaporated, and the residue crystallised from CH_2Cl_2/hexane: **12c** (1.20 g, 80%). White solid. M.p. 158–160° (CH_2Cl_2/hexane). TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): R_f 0.45. IR (KBr): 3430*s* (OH); 2960*m*, 2920*w* (sat. CH); 1630*s* (C=O); 1560*m* (C=C); 1475*s*, 1450*s*, 1375*m*, 1080*s*, 845*m*, 790*m*, 765, 715*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.15 (*t*, J = 7, 2 CH_3CH_2); 1.28 (*t*, J = 7, 2 CH_3CH_2); 2.66 (*s*, CH_3–C(6')); 3.25 (*q*, J = 7, CH_3CH_2); 3.57 (*q*, J = 7, 2 CH_3CH_2); 4.85 (*s*, CH_2OH); 7.18 (*d*, J = 0.9), 7.25 (*d*, J = 1.4, H–C(5), H–C(5')); 8.10, 8.36 (2*s*, H–C(3), H–C(3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.01, 14.34 (CH_3CH_2); 24.56 (CH_3–C(6')); 39.76, 42.13 (CH_3CH_2); 64.02 (CH_2OH); 115.11, 117.09, 118.43, 121.28 (C(3), C(3'), C(5), C(5')); 144.86, 146.00, 154.77, 155.50, 158.25, 160.98 (C(2), C(4), C(6), C(2'), C(4'), C(6')); 169 (C=O). EI-MS (70 eV): 398.50 (M^+). Anal. calc. for $C_{22}H_{30}N_4O_3$ (398.49): C 66.30, H 7.59, N 14.06; found: C 66.25, H 7.82, N 13.75.

N,N,N',N'-Tetraethyl-6,6'-bis(hydroxymethyl)-2,2'-bipyridine-4,4'-dicarboxamide (**13c**). At r.t., **9c** (3.08 g, 7.40 mmol) was treated with $(CF_3CO)_2O$ (25 ml) for 1 h. The excess anhydride was evaporated and the crude bis(trifluoroacetate) **11c** (yellow solid) dissolved in THF (20 ml) and treated with sat. aq. $NaHCO_3$ soln. (30 ml) at r.t. for 1 h. The THF was evaporated and the product extracted twice with $CHCl_3$ (100 ml). The combined org. layer was dried ($MgSO_4$) and evaporated and the residue crystallised from $CHCl_3$/hexane: 1.95 g (63%) of **13c**. White solid. M.p. 184–186° (acetone/Et_2O). TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): R_f 0.1. IR (KBr): 3440*s* (OH); 3060*w* (C=CH); 2970*m*, 2920*m* (sat. CH); 1620*s* (C=O); 1550*m* (C=C); 1480*s*, 1450*s*, 1375*m*, 1065*s*, 840*m*, 790*m*, 760*m*, 710*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.14 (*t*, J = 7, 2 CH_3CH_2); 1.28 (*t*, J = 7, 2 CH_3CH_2); 3.24 (*q*, J = 7, 2 CH_3CH_2); 3.58 (*q*, J = 7, 2 CH_3CH_2); 4.86 (*s*, 2 CH_2OH); 7.30 (*s*, 2 H, H–C(5,5')); 8.26 (*s*, 2 H, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.84, 14.22 (CH_3CH_2); 39.50, 42.30 (CH_3CH_2); 64.37 (CH_2OH); 116.52, 117.87,

(C(3,3'), C(5,5')); 146.03 (C(4,4')); 153.97 (C(2,2')); 160.35 (C(6,6')); 168.81 (C=O). EI-MS (70 eV): 414 (M^+). Anal. calc. for $C_{22}H_{30}N_4O_4$ (414.50): C 63.75, H 7.30, N 13.52; found: C 63.53, H 7.50, N 13.31.

*6-(Bromomethyl)-*N,N,N',N'*-tetraethyl-6'-methyl-2,2'-bipyridine-4,4'-dicarboxamide* (**14c**). A stirred soln. of **12c** (880 mg, 2.21 mmol) in CH_2Cl_2 (50 ml) at 0° was treated successively with Et_3N (2.0 ml, 14.2 mmol) and MsCl (0.50 ml, 6.46 mmol). After 1 h at 0° (TLC (Al_2O_3, CH_2Cl_2/MeOH 95:5): no **12c** left), the mixture was washed with H_2O (100 ml), dried ($CaCl_2$), and evaporated. To the crude dimesylate (brown oily residue) in THF (40 ml), anh. LiBr (2.00 g, 23.4 mmol) was added under stirring and the mixture heated to 40° for 1 h. After evaporation, the crude product was partitioned between CH_2Cl_2/H_2O 1:1 (100 ml). The aq. layer was separated and extracted with CH_2Cl_2 (100 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the crude product purified by CC (Al_2O_3, CH_2Cl_2/MeOH 99:1): 730 mg (79%) of **14c**. White solid. M.p. 120–122° (acetone). TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.65. IR (KBr): 3060*w*, 3040*w* (C=CH); 2970*m*, 2920*w* (sat. CH); 1635*s* (C=O); 1550*m* (C=C); 1470*s*, 790*m*, 760*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.17 (*t*, J = 7.4, 2 CH_3CH_2); 1.29 (*t*, J = 7.4, 2 CH_3CH_2); 2.65 (*s*, CH_3–C(6')); 3.26 (*q*, J = 7.4, 2 CH_3CH_2); 3.58 (*q*, J = 7, 2 CH_3CH_2); 4.62 (*s*, CH_2Br); 7.18, 7.45, 8.26, 8.38 (4*s*, H of bpy). Anal. calc. for $C_{22}H_{29}BrN_4O_2$ (461.19): C 57.26, H 6.33, N 12.14; found: C 57.39, H 6.49, N 11.86.

*6,6'-Bis(bromomethyl)-*N,N,N',N'*-tetraethyl-2,2'-bipyridine-4,4'-dicarboxamide* (**15c**). A stirred soln. of **13c** (800 mg, 1.93 mmol) in CH_2Cl_2 (50 ml) at 0° was treated successively with Et_3N (3.0 ml, 21.7 mmol) and MsCl (0.75 ml, 9.67 mmol). After 1 h at 0° (TLC (Al_2O_3, CH_2Cl_2/MeOH 96:4): no **13c** left), the mixture was washed with H_2O (100 ml), dried ($MgSO_4$) and evaporated. To the crude dimesylate (brown oily residue) in THF (50 ml), anh. LiBr (1.50 g, 17.5 mmol) was added under stirring and the mixture heated to 40° for 1 h. After evaporation, the crude product was partitioned between CH_2Cl_2/H_2O 1:1 (200 ml), the aq. layer separated and extracted with CH_2Cl_2 (100 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the crude product purified by CC (silica gel, CH_2Cl_2/MeOH 99.5:0.5): 730 mg (70%) of **15c**. White solid. M.p. 172–174° (CH_2Cl_2/MeOH): TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.65. IR (KBr): 3060*w*, 3040*w* (C=CH); 2970*m*, 2920*w* (sat. CH); 1635*s* (C=O); 1550*m* (C=C); 1470*s*, 1450*m*, 1375*m*, 850*m*, 790*m*, 760*m*, 720*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.19 (*t*, J = 7.4, 2 CH_3CH_2); 1.30 (*t*, J = 7.4, 2 CH_3CH_2); 3.26 (*q*, J = 7.4, 2 CH_3CH_2); 3.58 (*q*, J = 7, 2 CH_3CH_2); 4.62 (*s*, CH_2Br); 7.48 (*s*, 2 H, H–C(5,5')); 8.40 (*s*, 2 H, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.86, 14.23 (CH_3CH_2); 33.42 (CH_2Br); 39.48, 43.32 (CH_3CH_2); 117.56 (C(5,5')); 121.00 (C(3,3')); 146.77 (C(4,4')); 155.10 (C(2,2')); 156.99 (C(6,6')); 168.36 (C=O). EI-MS (70 eV): 540 (M^+). Anal. calc. for $C_{22}H_{28}Br_2N_4O_2$ (540.30): C 48.90, H 5.22, N 10.37; found: C 48.71, H 5.35, N 9.88.

N,N,N',N',N'',N'',N''',N'''*-Octaethyl-6',6'''-dimethyl-6,6''-[oxybis(methylene)]bis[2,2'-bipyridine]-4,4',4'',4'''-tetracarboxamide* (**2c**). To a stirred soln. of **12c** (100 mg, 0.29 mmol) in THF (20 ml) at 0°, NaH (15 mg, 0.35 mmol) was added. The soln. was allowed to warm to r.t. within 60 min. After addition of **14c** (120 mg, 0.29 mmol), the mixture was stirred at 40° for 12 h (TLC monitoring (Al_2O_3, CH_2Cl_2/MeOH 98:2)). Then, H_2O (5 ml) was added, and the solvents were evaporated. The crude product was partitioned between H_2O/CH_2Cl_2 1:1 (40 ml), the org. phase separated, the aq. phase extracted with CH_2Cl_2 (2 × 20 ml), the combined org. layer dried (Na_2SO_4) and evaporated, and the residue purified by CC (Al_2O_3, CH_2Cl_2/MeOH 98:2): 163 mg (72%) of **2c**. White solid. M.p. 186–188° (acetone). TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.65. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.03–1.18 (*m*, 4 CH_3CH_2); 1.21–1.36 (*m*, 4 CH_3CH_2); 2.65 (*s*, 6 H, CH_3–C(6',6''')); 3.15–3.31 (*m*, 4 CH_3CH_2); 3.50–3.66 (*m*, 4 CH_3CH_2); 4.91 (*s*, CH_2OCH_2); 7.15, 7.54, 8.21, 8.38 (4*s*, 8 H of bpy). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.82, 14.20 (CH_3CH_2); 24.50 (CH_3–C(6',6''')); 39.31, 43.29 (CH_3CH_2); 73.79 (CH_2O); 115.32, 116.97, 118.08, (CH of bpy); 146.04, 146.34 (C(4,4''), C(4',4''')); 155.11, 155.29, 158.34, 158.62 (C of bpy); 168.97 (C=O). FAB-MS: 779.5 ($[M + H]^+$). Anal. calc. for $C_{44}H_{58}N_8O_5$ (778.97): C 67.84, H 7.50, N 14.39; found: C 68.02, H 7.63, N 14.43.

*6,6''-{[4,4'-Bis(diethylcarbamoyl)-2,2'-bipyridine-6,6'-diyl]bis(methyleneoxymethylene)}-*N,N,N',N',N'',N''',N'''*-octaethyl-6',6'''-dimethylbis[2,2'-bipyridine]-4,4',4'',4'''-tetracarboxamide* (**3c**). To a stirred soln. of **12c** (933 mg, 2.34 mmol) in THF (200 ml) at 0°, NaH (101 mg, 2.53 mmol) was added. The resulting soln. was allowed to warm to r.t. during 70 min. After addition of **15c** (506 mg, 0.936 mmol), the mixture was stirred at 40° for 12 h (TLC monitoring (alumina, CH_2Cl_2/MeOH 98:2)). Then, H_2O (30 ml) was added, and the solvents were evaporated. The crude product was partitioned between H_2O/CH_2Cl_2 1:1 (200 ml). The org. phase was separated, the aq. phase extracted with CH_2Cl_2 (2 × 100 ml), the combined org. layer dried (Na_2SO_4), filtered, and evaporated: 1.39 g of crude product. The excess of **12c** was separated by CC (100 g of alumina CH_2Cl_2/MeOH 98:2): non polar 1st fraction and **12c** (250 mg, 0.627 mmol) as the 2nd fraction. Purification of the 1st fraction by CC (silica gel, CH_2Cl_2/MeOH 97:3) afforded 10 mg (0.012 mmol) of **16c** and 840 mg (0.715 mmol, 76%) of **3c** as a white solid. M.p. 230–231° (acetone). TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.65. UV (MeCN/$CHCl_3$ 97:3): 292 (43100). IR (KBr): 2970*m*, 2920*w* (sat. CH); 1630*s* (C=O); 1550*m* (C=C); 1470*s*, 1450*m*, 1370*m*, 1100*m* (C–O); 800*m*, 755*m*, 720*m*, 620*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.03–1.18 (*m*, 6 CH_3CH_2); 1.21–1.36 (*m*, 6 CH_3CH_2); 2.69 (*s*, CH_3–C(6',6''')); 3.15–3.31 (*m*, 6 CH_3CH_2); 3.50–3.66 (*m*, 6 CH_3CH_2); 4.91 (*s*, 2 CH_2OCH_2); 7.19 (*s*, 2 H,

H–C(5′,5‴)); 7.56 (*s*, 4 H, H–C(5,5″), H–C(5^{IV},5^{V})); 8.21 (*d*, *J* = 1.0, 2 H, H–C(3′,3‴)); 8.33, 8.39 (2*d*, *J* = 1.0, 4 H, H–C(3,3″), H–C(3^{IV},3^{V})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.83, 14.22 (CH_3CH_2); 24.50 (CH_3–C(6′,6‴)); 39.32, 43.28 (CH_3CH_2); 73.77 (CH_2O); 115.35, 116.94, 117.10, 118.06, 118.17, 120.35 (CH of bpy); 146.01, 146.34 (C(4,4″), C(4′,4‴), C(4^{IV},4^{V})); 155.12, 155.29, 158.53, 158.61 (C(2,2″), C(6,6″), C(2′,2‴), C(6′,6‴), C(2^{IV},2^{V}), C(6^{IV},6^{V})); 168.94 (C=O). FAB-MS: 1175.5 ([*M* + H]$^+$). Anal. calc. for $C_{54}H_{86}N_{12}O_8$ (1175.49): C 67.40, H 7.37, N 14.30; found: C 67.14, H 7.20, N 13.96.

6′-(Bromomethyl)-N,N,N′,N′,N″,N″,N‴,N‴*-octaethyl-6‴-methyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxamide* (**16c**). To a stirred soln. of **12c** (265 mg, 0.665 mmol) in THF (50 ml) at 0°, NaH (22 mg, 0.925 mmol) was added. After 1 h at r.t., **15c** (380 mg, 0.703 mmol) was added. The soln. was stirred at r.t. for 24 h. Addition of MeOH (5.0 ml) and evaporation afforded a yellow oily residue which was purified by FC (silica gel, CH_2Cl_2/MeOH 98:2→95:5). Crystallisation from acetone gave 208 mg (36%) of **16c** as a white solid. A second fraction of the CC gave 219 mg (0.186 mmol) of the more polar **3c**. **16c**: M.p. 91–93°. TLC (Al_2O_3, CH_2Cl_2/MeOH 98:2): R_f 0.35. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.03–1.16 (*m*, 4 CH_3CH_2); 1.21–1.38 (*m*, 4 CH_3CH_2); 2.69 (*s*, CH_3–C(6‴)); 3.17–3.35 (*m*, 4 CH_3CH_2); 3.50–3.66 (*m*, 4 CH_3CH_2); 4.62 (*s*, CH_2Br); 4.91 (*s*, CH_2OCH_2); 7.19, 7.46, 7.56 (3*s*, 4 H, H–C(5,5″), H–C(5′,5‴)); 8.21, 8.33, 8.39 (3*s*, 4 H, H–C(3,3″), H–C(3′,3‴)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.99, 14.36 (CH_3CH_2); 24.68 (CH_3–C(6‴)); 33.61 (CH_2Br); 39.50, 43.45 (CH_3CH_2); 73.86 (CH_2O); 115.46, 117.23, 117.49, 118.21, 118.59, 120.64, 120.90, (CH of bpy); 145.82, 146.00 (C(4′,4″), C(4′,4‴)); 154.89, 155.63, 158.65, 158.83 (C of bpy); 168.57, 169.05 (C=O). Anal. calc. for $C_{44}H_{61}BrN_8O_4 \cdot 3H_2O$ (911.93): C 57.94, H 6.96, N 12.28; found: C 57.37, H 7.06, N 12.24.

N,N,N′,N′,N″,N″,N‴,N‴*-Octaethyl-6′-(hydroxymethyl)-6‴-methyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxamide* (**17c**). A stirred soln. of **16c** (220 mg, 0.26 mmol) in DMF (20 ml) was treated with NaOAc (220 mg, 2.90 mmol) at 110° for 30 min. The DMF was evaporated, the residue partitioned between H_2O/CH_2Cl_2 2:3 (50 ml), the org. layer evaporated, and the resulting dimer monoacetate in THF (30 ml) treated with a soln. of Na_2CO_3 (420 mg) in H_2O (30 ml) at r.t. for 20 h. After evaporation of the THF, the precipitate was filtered off and dried *in vacuo*: 113 mg (55%) of **17c**. White solid M.p. 176–178°. TLC (Al_2O_3, $CHCl_3$/MeOH 95:5): R_f 0.40. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.07–1.16 (*m*, 4 CH_3CH_2); 1.21–1.38 (*m*, 4 CH_3CH_2); 2.64 (*s*, CH_3–C(6‴)); 3.17–3.35 (*m*, 4 CH_3CH_2); 3.50–3.66 (*m*, 4 CH_3CH_2); 4.85 (*s*, CH_2OH); 4.91 (*s*, CH_2OCH_2); 7.16, 7.54, 7.57 (3*s*, 4 H, H–C(5,5″), H–C(5′,5‴)); 8.19, 8.32, 8.35 (3*s*, 4 H, H–C(3,3″), H–C(3′,3‴)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.80, 14.21 (CH_3CH_2); 24.50 (CH_3–C(6‴)); 39.31, 43.29 (CH_3CH_2); 64.0 (CH_2OH); 73.8 (CH_2OCH_2); 115.31, 116.92, 117.10, 118.08, 118.12, 120.33 (CH of bpy); 146.01, 146.32 (C(4, 4″), C(4′, 4‴)); 155.10, 155.29, 158.51, 158.63 (C of bpy); 168.93 (C=O). Anal. calc. for $C_{44}H_{58}N_8O_6$ (794.97): C 66.47, H 7.35, N 14.09; found: C 65.91, H 7.20, N 13.28.

N,N,N′,N′,N″,N″,N‴,N‴-*Octaethyl-6′,6‴-dimethyl-6,6″-{[oxybis(methylene)]bis[4,4′-bis(diethylcarbamoyl)-2,2′-bipyridine-6′,6-diyl]bis(methyleneoxymethylene)}bis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxamide* (**4c**). To a stirred soln. of **17c** (113 mg, 0.14 mmol) in THF (40 ml) at 0°, NaH (6.5 mg, 0.27 mmol) was added and the soln. allowed to warm to r.t. within 1 h. After addition of **16c** (122 mg, 0.14 mmol), the mixture was stirred for 20 h at 40° (TLC monitoring (Al_2O_3, CH_2Cl_2/MeOH 98:2)). Then, H_2O (2 ml) was added and the mixture evaporated. The crude product was partitioned between CH_2Cl_2/H_2O 1:1 (60 ml), the org. layer dried ($MgSO_4$), and the crude product purified by CC (Al_2O_3, CH_2Cl_2/MeOH 98:2): 124 mg (56%) of **4c**. White solid. M.p. 246–248°. TLC (Al_2O_3, $CHCl_3$/MeOH 95:5): R_f 0.50. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.03–1.16 (*m*, 8 CH_3CH_2); 1.21–1.38 (*m*, 8 CH_3CH_2); 2.69 (*s*, 6 H, CH_3–C(6′,6‴)); 3.17–3.35 (*m*, 8 CH_3CH_2); 3.50–3.66 (*m*, 8 CH_3CH_2); 4.91 (*s*, 3 CH_2OCH_2); 7.19 (*s*, 2 H, H–C(5′,5‴)); 7.56 (*s*, 6 H, H–C(5,5″), H–C(5^{IV},5^{VI}), H–C(5^{V},5^{VII})); 8.21 (*s*, 2 H, H–C(3′,3‴)); 8.33 (*s*, 2 H, H–C(3,3″)); 8.39 (*s*, 4 H, H–C(3^{IV},3^{VI}), H–C(3^{V},3^{VII})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 13.00, 14.39 (CH_3CH_2); 24.71 (CH_3–C(6′,6‴)); 39.52, 43.40 (CH_3CH_2); 73.94 (CH_2OCH_2); 115.39, 117.12, 117.19, 118.10, 118.38, 120.58 (CH of bpy); 146.51 (C(4,4″), C(4′,4‴), C(4^{IV},4^{VI}), C(4^{V},4^{VII})); 155.30, 158.62 (C of bpy); 169.11 (C=O). FAB-MS (pos. mode): 1571.9 (calc. 1571.83). Anal. calc. for $C_{88}H_{114}N_{16}O_{11}$ (1607.86): C 65.73, H 7.39, N 13.93; found: C 65.39, H 7.37, N 13.75.

6,6″-{[4,4′-Bis(diethylcarbamoyl)-2,2′-bipyridine-6,6′-diyl]bis(methyleneoxymethylene)bis[4,4′-bis(diethylcarbamoyl)-2,2′-bipyridine-6′,6-diyl]bis(methyleneoxymethylene)}-N,N,N′,N′,N″,N″,N‴,N‴-*octaethyl-6′,6‴-dimethylbis[2,2′-bipyridine]-4,4′,4″,4‴-tetracarboxamide* (**5c**). To a stirred soln. of **17c** (100 mg, 0.13 mmol) in THF (10 ml), NaH (7 mg, 0.18 mmol) was added. After 1 h at r.t., **15c** (34 mg, 0.065 mmol) was added, the soln. stirred for 15 h at 40° and evaporated and the yellow solid purified by FC (silica gel, CH_2Cl_2/MeOH 98:2→90:10): 94 mg (74%) of **5c**. White solid. M.p. 254–256° (dec.; $CHCl_3$/MeOH). TLC (Al_2O_3, $CHCl_3$/MeOH 95:5): R_f 0.40. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10–1.16 (*m*, 10 CH_3CH_2); 1.21–1.38 (*m*, 10 CH_3CH_2); 2.69 (*s*, 6 H, CH_3–C(6′, 6‴)); 3.17–3.35 (*m*, 10 CH_3CH_2); 3.50–3.66 (*m*, 10 CH_3CH_2); 4.91 (*s*, 4 CH_2OCH_2); 7.19 (*s*, 2 H, H–C(5′,5‴)); 7.56 (*s*, 8 H, H–C(5,5″), H–C(5^{IV},5^{VI}), H–C(5^{V},5^{VII}), H–C(5^{VIII},5^{IX})); 8.21 (*s*, 2 H, H–C(3′,3‴)); 8.33 (*s*, 6 H, H–C(3,3″),

H–C(3^{IV},3^{VI}), H–C(3^{V},3^{VII})); 8.39 (*s*, H–C(3^{VIII},3^{IX})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 12.99, 14.38 (CH_3CH_2); 24.76 (CH_3–C(6′,6‴)); 39.52, 43.44 (CH_3CH_2); 73.97 (CH_2O); 115.37, 117.12, 118.16, 118.35, 120.58 (CH of bpy); 145.96, 146.51 (C(4,4″), C(4′,4‴), C(4^{IV},4^{VII}), C(4^{V},4^{VI}), C(4^{VIII},4^{IX})); 155.31, 155.75, 158.75 (C(2,2″), C(6,6″), C(6′,6‴), C(2^{IV},2^{VI}), C(6^{IV},6^{VI}), C(2^{V},2^{VII}), C(6^{V},6^{VII}), C(2^{VIII},2^{IX}), C(6^{VIII},6^{IX})); 169.09 (C=O). FAB-MS (pos. mode): 1968.6 (calc. 1968.41). Anal. calc. for $C_{66}H_{80}N_6O_{14}\cdot 4H_2O$ (2040.47): C 64.74, H 7.41, N 13.73; found: C 64.42, H 7.17, N 13.10.

5. *Elongated Ester-Substituted Oligobipyridines (***d** and **e** Series). *6,6′-Dimethyl-2,2′-bipyridine-4,4′-dimethanol* (**7a**). To a stirred suspension of **6** (16.0 g, 53.3 mmol) in THF (1 l) at −40°, $LiAlH_4$ (2.03 g, 53.5 mmol) was added. Within 1 h, the temp. of the mixture was raised to −10°, and more $LiAlH_4$ (2.03 g, 53.3 mmol) was added. Stirring for 2 h at r.t. completed the reaction (TLC control (Al_2O_3, $CHCl_3$/MeOH 95:5)). At 0°, H_2O (4.0 ml) was added dropwise very carefully followed by 2N aq. NaOH (8.0 ml). After 15 min, the green/white suspension was refluxed for 5 min and stirred at r.t. for 2 h. The white $Al(OH)_3$ precipitate was filtered off. Evaporation of the solvent and recrystallisation of the crude product from $CHCl_3$/Et_2O gave **7a** (12.4 g, 50.7 mmol). White solid. M.p. 152°. TLC (Al_2O_3, $CHCl_3$/MeOH 95:5): R_f 0.40. IR (KBr): 3290*s* (br. OH); 1600*s*, 1560*s*, 1400*s*, 1180*m*, 850*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.58 (*s*, 6 H, CH_3–C(6,6′)); 4.67 (*s*, 2 CH_2O); 7.26 (*s*, 2 H, H–C(5,5′)); 7.98 (*s*, 2 H, H–C(3,3′)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.61 (CH_3–C(6,6′)); 64.08 (CH_2O); 118.14 (C(5,5′)); 122.32 (C(3,3′)); 154.49, 157.50, 159.83 (C(2,2′), C(4,4′), C(6,6′)). Anal. calc. for $C_{14}H_{16}N_2O_2$ (244.29): C 68.82, H 6.60, N 11.47; found: C 68.86, H 6.69, N 11.46.

6,6′-Dimethyl-2,2′-bipyridine-4,4′-dicarbaldehyde (**7b**). Oxalyl chloride (8.0 ml, 92.0 mmol) was added to CH_2Cl_2 (400 ml) freshly filtered over basic aluminium oxide (act. I, 50 g) at −60°. N_2 was passed through the apparatus while DMSO (10.9 ml, 153.6 mmol) in CH_2Cl_2 (20 ml) was added dropwise over 5 min. After 10 min, a soln. of **7a** (7.50 g, 30.7 mmol) in THF (400 ml) was added within 15 min. The temp. was kept under −40° during this addition. After 45 min at −50°, Et_3N (40.0 ml, 284.6 mmol) was added dropwise over 5 min. The temp. was raised in 1 h to 0°. Addition of $CHCl_3$ (600 ml) and half-sat. aq. NH_4Cl soln. (600 ml) gave two phases. The org. layer was separated and the aq. layer washed twice with $CHCl_3$ (200 ml). Washing the combined org. layer with sat. aq. NaCl soln. (500 ml) and drying ($MgSO_4$) yielded, after evaporation, a light brown solid, which was purified by crystallisation from $CHCl_3$/Et_2O: 6.12 g (83%) of **7b**. White powder. M.p. 233°. TLC (Al_2O_3, $CHCl_3$/MeOH 98:2): R_f 0.80. IR (KBr): 3062*w* (C=C); 2917*w* (sat. CH); 2851*m* (sat. CH); 2731*w* (CHO); 1596*s* (C=C); 1383*m*, 1260*s*, 1169*s*, 877*m*, 674*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.74 (*s*, 6 H, CH_3–C(6,6′)); 7.59 (*s*, 2 H, H–C(5,5′)); 8.66 (*s*, 2 H, H–C(3,3′)); 10.15 (*s*, 2 CHO). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.62 (CH_3–C(6,6′)); 118.01 (C(5,5′)); 121.34 (C(3,3′)); 143.02, 156.56, 159.91 (C(2,2′), C(4,4′), C(6,6′)); 192.05 (CHO). Anal. calc. for $C_{14}H_{12}N_2O_2$ (240.26): C 66.98, H 5.00, N 11.66; found: C 66.93, H 5.09, N 11.42.

*(*E,E*)-Di(*tert*-butyl) 6,6′-Dimethyl-2,2′-bipyridine-4,4′-diacrylate* (**7c**). Dicarbaldehyde **7b** (1.72 g, 7.16 mmol) and {[(*tert*-butoxy)carbonyl]methylidene}triphenylphosphorane (6.74 g, 17.9 mmol) were dissolved in toluene (150 ml). After 6 h at 70° (TLC (Al_2O_3, $CHCl_3$): no **7b** left), the solvent was evaporated and the remaining crude product filtered over Al_2O_3 (50 g, $CHCl_3$) and purified by CC (200 g of Al_2O_3, CH_2Cl_2): 2.53 g (80%) of **7c**. White solid. M.p. 211° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.80. UV ($CHCl_3$): 319 (10870), 256 (42940). IR (KBr): 2920*w* (sat. CH); 1700*s* (C=O); 1640*m* (C=C, olef.); 1590, 1555*s* (C=C, arene); 1390, 1365*s* (*t*-Bu ester); 1315*s*, 1255*s*, 1150*s*, 985*m* ((*E*)-olefin); 855*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.55 (*s*, 2 *t*-Bu); 2.66 (*s*, 6 H, CH_3–C(6,6′)); 6.64 (*d*, *J* = 16.0, 2 H, H–C(α,α′)); 7.23 (*s*, 2 H, H–C(5,5′)); 7.58 (*d*, *J* = 16.0, 2 H, H–C(β, β′)); 8.32 (*s*, 2 H, H–C(3,3′)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.61 (CH_3–C(6,6′)); 28.17 ((CH_3)$_3$C); 81.12 ((CH_3)$_3C$); 116.52 (C(5,5′)); 121.66 (C(3,3′)); 124.55 (C(β,β′)); 141.26 (C(α,α′)); 143.11, 156.16, 158.82 (C(2,2′), C(4,4′), C(6,6′)); 165.54 (C=O). Anal. calc. for $C_{26}H_{32}N_2O_4$ (436.54): C 71.53, H 7.39, N 6.42; found: C 71.51, H 7.45, N 6.20.

*Di(*tert*-butyl) 6,6′-Dimehtyl-2,2′-bipyridine-4,4′-dipropionate* (**1d**). To a soln. of **7c** (2.21 g, 5.07 mmol) in toluene/EtOH 1:1 (200 ml), 5% Pd/C (300 mg) was added. The mixture was heated under H_2 (1 atm.) to 60°. After 2 h (TLC monitoring (Al_2O_3, $CHCl_3$)); the mixture was cooled to r.t., washed with N_2, and filtered over *Celite*. Evaporation and CC (120 g of Al_2O_3, $CHCl_3$) gave 1.89 g (85%) of **1d**. White solid. M.p. 114° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.75. UV ($CHCl_3$): 292 (16080). IR (KBr): 2900*w* (sat. CH); 1705*s* (C=O); 1590, 1555*s* (C=C, arene); 1390, 1365*s* (*t*-Bu ester), 1300*m*, 1260*m*, 1140*s* (C–O); 875*m*, 850*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.43 (*s*, 2 *t*-Bu); 2.58 (*s*, 6 H, CH_3–C(6,6′)); 2.57–2.64 (*m*, 2 H, H–C(β,β′)); 2.91–2.98 (*m*, 2 H, H–C(α,α′)); 7.00 (*s*, 2 H, H–C(5,5′)); 8.03 (*s*, H–C(3,3′)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.53 (CH_3–C(6,6′)); 28.05 ((CH_3)$_3$C); 30.45 (C(β,β′)); 35.85 (C(α,α′)); 80.64 ((CH_3)$_3C$); 118.25 (C(5,5′)); 123.12 (C(3,3′)); 150.64, 155.97, 157.80 (C(2,2′), C(4,4′), C(6,6′)); 171.80 (C=O). Anal. calc. for $C_{26}H_{36}N_2O_4$ (440.57): C 70.88, H 8.24, N 6.36; found: C 70.96, H 8.46, N 6.11.

*4,4'-Bis{2-[(*tert*-butoxy)carbonyl]ethyl}-6,6'-dimethyl-2,2'-bipyridine 1-Oxide* (**8d**) *and 4,4'-Bis{2-[(*tert*-butoxy)carbonyl]ethyl}-6,6'-dimethyl-2,2'-bipyridine 1,1'-Dioxide* (**9d**). To a soln. of **1d** (5.71 g, 12.9 mmol) in $CHCl_3$ (100 ml) at 0°, a soln. of 3-$ClC_6H_4CO_3H$ (2.45 g, 14.2 mmol) in $CHCl_3$ (200 ml) was added dropwise within 30 min. After 30 min at 0° and 15 min at r.t. (TLC monitoring (Al_2O_3, $CHCl_3$/MeOH 98:2)), the solvent was evaporated and the crude product purified by CC (200 g of Al_2O_3, CH_2Cl_2, then $CHCl_3$/MeOH 98:2): 4.11 g (70%) of **8d** and 0.98 g (16%) of **9d** both white crystalline solids.

Data of **8d**: M.p. 132° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$/MeOH 98:2): R_f 0.75. IR (KBr): 3055*w* (C=C); 2980*w* (sat. CH); 2916*w* (sat. CH); 1720*s* (C=O); 1550*m* (C=C, arene); 1434*s*, 1373, 1334*s* (*t*-Bu ester); 1253*s*, 1219*s* (*N*-oxide); 1149*s* (C–O); 883*m*, 820*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.39 (*s*, 2 *t*-Bu); 2.52 (*s*, CH_3–C(6)); 2.54 (CH_3–C(6')); 2.52–2.60 (*m*, 2 H–C(*β*), 2 H–C(*β'*)); 2.86–2.94 (*m*, 2 H–C(α), 2 H–C(α')); 7.02 (*s*, H–C(5')); 7.10 (*d*, *J*(H–C(5),H–C(3)) = 2.5, H–C(5)); 7.80 (*d*, *J*(H–C(3),H–C(5)) = 2.5, H–C(3)); 8.47 (*s*, H–C(3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 18.38 (CH_3–C(6)); 24.39 (CH_3–C(6')); 28.00 ((CH_3)$_3$C); 29.58, 30.39 (C(*β*), C(*β'*)); 35.63, 35.82, (C(α), C(α')); 80.55, 80.84 ((CH_3)$_3C$); 122.55, 123.73, 125.42, 125.64 (C(3), C(3'), C(5), C(5')); 138.77, 146.90, 149.14, 149.66, 150.15, 157.86 (C(2), C(2'), C(4), C(4'), C(6), C(6')); 171.44, 171.69 (C=O). Anal. calc. for $C_{26}H_{36}N_2O_5$ (456.57): C 68.39, H 7.95, N 6.14; found: C 68.20, H 8.13, N 6.10.

Data of **9d**: M.p. 165° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$/MeOH 98:2): R_f 0.45. IR (KBr): 3055*w* (C=C); 2980*w* (sat. CH); 2916*w* (sat. CH); 1720*s* (C=O); 1550*m* (C=C, arene); 1434*s*, 1373, 1334*s* (*t*-Bu ester); 1253*s*, 1219*s* (*N*-oxide); 1149*s* (C–O); 883*m*, 820*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.36 (*s*, 2 *t*-Bu); 2.47 (*s*, CH_3–C(6,6')); 2.46–2.53 (*m*, 4 H, 2 H–C(*β*,*β'*)); 2.82 (*t*, *J*(H–C(α), H–C(*β*) = 7.4, 4 H, 2 H–C(α,α')); 7.14 (*s*, H–C(3,3'), H–C(5,5')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 17.77 (CH_3–C(6,6')); 27.88 ((CH_3)$_3$C); 29.24 (C(*β*, *β'*)); 35.39 (C(α, α')); 80.76 ((CH_3)$_3C$); 125.11, 126.56 (C(3,3'), C(5,5')); 138.04, 142.67, 148.83 (C(2,2'), C(4,4'), C(6,6')); 171.21 (C=O). Anal. calc. for $C_{26}H_{36}N_2O_6$ (472.57): C 66.08, H 7.68, N 5.93; found: C 66.07, H 7.85, N 5.83.

*Di(*tert*-butyl) 6-(Acetoxymethyl)-6'-methyl-2,2'-bipyridine-4,4'-dipropionate* (**10d**). A stirred soln. of **8d** (2.77 g, 6.07 mmol) in Ac_2O (80 ml) was heated to 130° for 15 min. Evaporation and CC (150 g of Al_2O_3, $CHCl_3$) of the remaining yellow oil gave 2.13 g (70%) of **10d**. Colourless oil. TLC (Al_2O_3, $CHCl_3$): R_f 0.50. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.40 (*s*, 2 *t*-Bu); 2.17 (*s*, CH_3COO); 2.56 (*s*, CH_3–C(6')); 2.54–2.64 (*m*, 2 H–C(*β*), 2 H–C(*β'*)); 2.89–3.02 (*m*, 2 H–C(α), 2 H–C(α')); 5.24 (*s*, CH_2–C(6)); 6.99, 7.17 (2*s*, H–C(5), H–C(5')); 8.04, 8.18 (2*s*, H–C(3), H–C(3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 20.92 (CH_3COO); 24.39 (CH_3–C(6')); 27.97 ((CH_3)$_3$C); 30.37, 30.51 (C(*β*), C(*β'*)); 35.71 (C(α), C(α')); 67.00 (CH_2–C(6)); 80.59, 80.63 ((CH_3)$_3C$); 118.32, 120.11, 121.30, 123.38 (C(3), C(3'), C(5), C(5')); 150.68, 151.33, 155.17, 155.23, 156.07, 157.77 (C(2), C(2'), C(4), C(4'), C(6), C(6')); 171.53, 171.63 (C=O). Anal. calc. for $C_{28}H_{38}N_2O_6$ (498.60): C 67.44, H 7.68, N 5.62; found: C 67.27, H 7.63, N 5.40.

*Di(*tert*-butyl) 6-(Hydroxymethyl)-6'-methyl-2,2'-bipyridine-4,4'-dipropionate* (**12d**). To a soln. of **10d** (2.13 g, 4.27 mmol) in EtOH (200 ml), K_2CO_3 (1.00 g, 7.24 mmol) was added and stirred for 12 h at r.t. Evaporation and filtration of the remaining oil with $CHCl_3$/MeOH 98:2 over 50 g of Al_2O_3 gave the crude product which was purified by CC (100 g of Al_2O_3, $CHCl_3$): 1.45 g (74%) of **12d**. White solid. M.p. 74–75° ($CHCl_3$/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.10. IR (KBr): 3531*m* (OH); 3411*w* (OH); 2976*m* (sat. CH); 2933*w* (sat. CH); 1722*s* (C=O); 1597, 1564*s* (C=C, arene); 1389, 1367*s* (*t*-Bu ester); 1161*s* (C–O); 1072*m*, 876*m*, 847*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.42 (*s*, 2 *t*-Bu); 2.58 (*s*, CH_3–C(6')); 2.57–2.64 (*m*, 2 H–C(*β*), 2 H–C(*β'*)); 2.91–3.03 (*m*, 2 H–C(α), 2 H–C(α')); 4.11 (*t*, *J*(OH,CH_2–C(6)) = 3.5, OH); 4.77 (*d*, *J*(CH_2–C(6),OH) = 3.5, CH_2–C(6)); 7.02, 7.07 (2*s*, H–C(5), H–C(5')); 8.04, 8.18 (2*s*, H–C(3), H–C(3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.45 (CH_3–C(6')); 28.00 ((CH_3)$_3$C); 30.42, 30.47 (C(*β*), C(*β'*)); 35.68, 35.76 (C(α), C(α')); 63.92 (CH_2OH); 80.67, 80.73 ((CH_3)$_3C$); 118.15, 119.83, 120.09, 123.46 (C(3), C(3'), C(5), C(5')); 150.73, 151.46, 155.08, 157.92, 158.28 (C(2), C(2'), C(4), C(4'), C(6), C(6')); 171.57 (C=O). Anal. calc. for $C_{26}H_{36}N_2O_5$ (456.57): C 68.39, H 7.95, N 6.14; found: C 68.25, H 7.85, N 6.07.

*Di(*tert*-butyl) 6,6-Bis(acetoxymethyl)-2,2'-bipyridine-4,4'-dipropionate* (**11d**). A mixture of **9d** (915 mg, 1.94 mmol) in Ac_2O (15 ml) was heated to 130° for 15 min. After evaporation, the crude product was filtered over 50 g of Al_2O_3 with CH_2Cl_2. Crystallisation from hexane/Et_2O gave 816 mg (76%) of **11d**. White solid. M.p. 86° (Et_2O/hexane). TLC (Al_2O_3, $CHCl_3$): R_f 0.40. IR (KBr): 3080*w* (C=CH); 2975*m* (sat. CH); 2939*w* (sat. CH); 1740*s* (C=O, acetate); 1722*s* (C=O, *t*-Bu ester); 1596, 1561*s* (C=C, arene); 1371*s* (*t*-Bu ester); 1234*s*, 1146*s* (C–O); 1040*m*, 876*m*, 854*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.43 (*s*, 2 *t*-Bu); 2.19 (*s*, 2 CH_3COO); 2.62 (*t*, *J*(H–C(*β*),H–C(α)) = 7.6, 4 H, 2 H–C(*β*,*β'*)); (*t*, *J*(H–C(α),H–C(*β*)) = 7.6, 4 H, 2 H–C(α,α')); 5.26 (*s*, 4 H, CH_2–C(6,6')); 7.21 (*d*, *J*(H–C(5),H–C(3)) = 1.0, 2 H, H–C(5,5')); 8.21 (*d*, *J*(H–C(3),H–C(5)) = 1.0, 2 H, H–C(3,3')). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 21.03 (CH_3COO); 28.06 ((CH_3)$_3$C); 30.59 (C(*β*,*β'*)); 35.76 (C(α,α')); 67.01 (CH_2–C(6,6')); 80.81 ((CH_3)$_3C$); 120.32, 121.70 (C(3,3'), C(5,5')); 151.52, 155.29, 155.54 (C(2,2', C(4,4'), C(6,6')); 170.68 (C=O, acetate); 171.69 (C=O, *t*-Bu ester). Anal. calc. for $C_{30}H_{40}N_2O_8$ (556.05): C 64.73, H 7.24, N 5.03; found: C 65.00, H 7.47, N 4.78.

*Di(*tert*-butyl) 6,6′-Bis(hydroxymethyl)-2,2′-bipyridine-4,4′-dipropionate* (**13d**). To a soln. of **11d** (2.59 g, 4.66 mmol) in EtOH (40 ml), K_2CO_3 (2.00 g, 14.47 mmol) was added and the mixture stirred for 12 h at r.t. Evaporation and CC (300 g of Al_2O_3, $CHCl_3$/MeOH 95:5) gave 1.72 g (78%) of **13d**. White solid. M.p. 81° (Et_2O/hexane). TLC (Al_2O_3, $CHCl_3$/MeOH 98:2): R_f 0.15. IR (KBr): 3509*m* (OH); 3427*m* (OH); 3096*w* (C=C); 2980*s* (sat. CH); 2928*m* (sat. CH); 1726*s* (C=O); 1596, 1564*s* (C=C, arene); 1367*s* (*t*-Bu ester); 1275*s*, 1149*s* (C–O); 1040*m*, 883*w*, 850*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.40 (*s*, 2 *t*-Bu); 2.61 (*t*, *J*(H–C(*β*),H–C(α)) = 7.3, 4 H, 2 H–C(*β*,*β*′)); 2.98 (*t*, *J*(H–C(α),H–C(*β*)) = 7.3, 4 H, 2 H–C(α,α′)); 4.02 (*s*, 2 OH); 4.78 (*s*, 4 H, CH_2–C(6,6′)); 7.10 (*s*, 2 H, H–C(5,5′)); 8.15 (*s*, 2 H, H–C(3,3′)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 28.00 ((CH_3)$_3$C); 30.47 (C(*β*,*β*′)); 35.62 (C(α,α′)); 63.95 (CH_2–C(6,6′)); 80.84 ((CH$_3$)$_3$*C*); 119.79, 120.49 (C(3,3′), C(5,5′)); 151.63, 154,28, 158.51 (C(2,2′), C(4,4′), C(6,6′)); 171.51 (C=O). Anal. calc. for $C_{26}H_{36}N_2O_6$ (472.57): C 66.08, H 7.68, N 5.93; found: C 66.23, H 7.50, N 5.94.

*Di(*tert*-butyl) 6,6′-Bis(bromomethyl)-2,2′-bipyridine-4,4′-dipropionate* (**15d**). A stirred suspension of **13d** (3.71 g, 7.85 mmol) in CH_2Cl_2 (150 ml) at 0° was treated successively with MsCl (2.50 ml, 31.4 mmol) and Et_3N (6.60 ml, 47.1 mmol). The resulting yellow soln. was allowed to warm to r.t., stirred for 15 min, then washed with sat. aq. NH_4Cl soln. (2 × 150 ml), dried ($MgSO_4$), and evaporated. To the crude dimesylate (brown oily residue) in THF (150 ml), anh. LiBr (5.00 g, 57.6 mmol) was added under stirring and the mixture heated to 50° for 30 min. After evaporation, the crude product was partitioned between Et_2O/aq. NH_4Cl soln. 2:1 (300 ml). The aq. layer was separated and extracted with Et_2O (100 ml), the combined org. layer dried ($MgSO_4$) and evaporated, and the residue purified by CC (Al_2O_3, hexane/AcOEt 4:1): 3.10 g (66%) of **15d**. White needles. M.p. 116° (Et_2O/hexane). TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.60. IR (KBr): 3074*w* (C=C); 2976*s* (sat. CH); 1722*s* (C=O); 1593, 1554*s* (C=C, arene); 1417*m*, 1392*m*, 1367*s* (*t*-Bu ester); 1244*s*, 1146*s* (C–O); 854*m*, 590*m* (C–Br). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.44 (*s*, 2 *t*-Bu); 2.65 (*t*, *J*(H–C(*β*),H–C(α)) = 7.6, 4 H, 2 H–C(*β*,*β*′)); 3.02 (*t*, *J*(H–C(α),H–C(*β*)) = 7.6, 4 H, 2 H–C(α, α′)); 4.61 (*s*, 4 H, CH_2–C(6,6′)); 7.33 (*s*, 2 H, H–C(5,5′)); 8.24 (*s*, 2 H, H–C(3,3′)). Anal. calc. for $C_{26}H_{34}Br_2N_2O_4$ (598.38): C 52.18, H 5.73, Br 26.71, N 4.68; found: C 52.68, H 5.73, Br 26.25, N 4.87.

*Tetra(*tert*-butyl) 6,6″-[(2,2′-Bipyridine-6,6′-diyl)bis(methyleneoxymethylene)]-6,6′-dimethylbis[2,2′-bipyridine]-4,4′4″,4‴-tetrapropionate* (**3d**). To a stirred soln. of **12d** (1.05 g, 2.30 mmol) in *t*-BuOH (100 ml) KO(*t*-Bu) (300 mg, 2.68 mmol) was added. The resulting yellow soln. was stirred at r.t. for 15 min. Then, **15a** (376 mg, 1.10 mmol) in CH_2Cl_2 (100 ml) was added. After 12 h, H_2O (3 ml) was added, the soln. evaporated, and the remaining oil filtered over 30 g of Al_2O_3 with $CHCl_3$. CC (100 g of Al_2O_3, hexane/AcOEt 4:1) of the crude product afforded 735 mg (61%) of **3d**. White solid. M.p. 48° (Et_2O/hexane). TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.10. UV ($CHCl_3$): 295 (47700). FT-IR (KBr): 3060*w* (C=CH); 2975, 2931*m* (sat. CH); 1725*s* (C=O); 1598*s*, 1554*m* (C=C); 1365*m* (*t*-Bu ester); 1159*s* (C–O); 870*m*, 855*m*, 798*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.41 (*s*, 2 *t*-Bu); 1.42 (*s*, 2 *t*-Bu); 2.59 (*s*, 6 H, CH_3–C(6′,6‴)); 2.55–2.68 (*m*, 8 H, 2 H–C(*β*,*β*″), 2 H–C(*β*′,*β*‴)); 2.90–3.06 (*m*, 8 H, 2 H–C(α,α″), 2 H–C(α′,α‴)); 4.87 (*s*, 4 H, OCH_2–C(6^{IV},6^{V})); 4.90 (*s*, 4 H, OCH_2–C(6,6′)); 7.01 (*s*, 2 H, H–C(5′,5‴)); 7.26 (*s*, 2 H, H–C(5,5″)); 7.58 (*d*, *J* = 7.6, 2 H, H–C(5^{IV},5^{V})); 7.85 (*t*, *J* = 7.6, 2 H, H–C(4^{IV},4^{V})); 8.04 (*s*, 2 H, H–C(3′, 3‴)); 8.17 (*s*, 2 H–C(3,3″)); 8.33 (*d*, *J* = 7.6, 2 H, H–C(3^{IV},3^{V})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.47 (CH_3–C(6′,6‴)); 28.05 ((CH_3)$_3$C); 30.47, 30.68, (C(*β*,*β*″), C(*β*′,*β*‴)); 35.84 (C(α,α″), C(α′,α‴)); 73.90, 73.99 (CH_2OCH_2); 80.69 ((CH$_3$)$_3$*C*); 118.39, 119.87, 121.08, 121.31, 123.36, 137.50, 151.31, 155.49, 157.83, 157.89 (bpy); 171.72 (C=O). FAB-MS (pos. mode): 1093.6 (calc. 1093.3). Anal. calc. for $C_{64}H_{80}N_6O_{10}$ (1093.33): C 70.30, H 7.38, N 7.69; found: C 70.40, H 7.66, N 7.53.

*Tetra(*tert*-butyl) 6,6″-{{4,4′-Bis{2-[(*tert*-butyl)carbonyl]ethyl}-2,2′-bipyridine-6,6′-diyl}bis(methyleneoxymethylene)}-6′,6‴-dimethylbis[2,2′-bipyridine]-4,4′,4″,4‴-tetrapropionate* (**3e**). To a stirred soln. of **12d** (740 mg, 1.62 mmol) in *t*-BuOH (50 ml), KO(*t*-Bu) (181 mg, 1.62 mmol) was added. The resulting yellow soln. was stirred at r.t. for 10 min. Then, **15d** (115 mg, 0.192 mmol) in CH_2Cl_2 (40 ml) was added. After 3 h at r.t. (TLC (Al_2O_3, $CHCl_3$): no **15d** left), H_2O (1 ml), was added and the soln. evaporated. The remaining oil was filtered over 30 g of Al_2O_3 with $CHCl_3$. CC (80 g of Al_2O_3, hexane/AcOEt 4:1) of the crude product afforded 130 mg (50%) of **3e**. White solid. M.p. 76° (Et_2O/hexane). TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.15. FT-IR (KBr): 3060*w* (C=CH); 2975, 2931*m* (sat. CH); 1725*s* (C=O); 1598*s*, 1554*m* (C=C); 1365*m* (*t*-Bu ester); 1159*s* (C–O); 870*m*, 855*m*, 798*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.41 (*s*, 3 *t*-Bu); 1.42 (*s*, 3 *t*-Bu); 2.59 (*s*, 6 H, CH_3–C(6′,6‴)); 2.55–2.68 (*m*, 12 H, 2 H–C(*β*,*β*″), 2 H–C(*β*′,*β*‴), 2 H–C(*β*^{IV},*β*^{V})); 2.90–3.07 (*m*, 12 H, 2 H–C(α,α″), 2 H–C(α′,α‴), 2 H–C(α^{IV},α^{V})); 4.86 (*s*, 2 CH_2OCH_2); 7.01 (*s*, 2 H, H–C(5′,5‴)); 7.42 (*s*, 4 H, H–C(5,5″), H–C(5^{IV},5^{V})); 8.05 (*s*, H–C(3′,3‴)); 8.17 (*s*, H–C(3,3″), H–C(3^{IV},3^{V})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.50 (CH_3–C(6′,6‴)); 28.05 ((CH_3)$_3$C); 30.47, 30.67, (C(*β*,*β*″), C(*β*,*β*‴), C(*β*^{IV},*β*^{V})); 35.82 (C(α,α″), C(α′,α‴), C(α^{IV},α^{V})); 74.00 (CH_2OCH_2); 80.67 ((CH$_3$)$_3$*C*); 119.91, 121.17, 151.36, 155.54, 157.91 (bpy); 171.66, 171.72 (C=O). Anal. calc. for $C_{78}H_{104}N_6O_{14}$ (1349.66): C 79.41, H 7.77, N 6.23; found: C 69.59, H 7.83, N 6.23.

*Di(*tert*-butyl) 6‴-(Bromomethyl)-6′-methyl-6,6″-[oxybis(methylene)]bis[2,2′-bipyridine]-4,4′-dipropionate* (**16d**). To a stirred soln. of **12d** (1.54 mg, 3.37 mmol) in *t*-BuOH (150 ml), KO(*t*-Bu) 447 mg, 4.00 mmol) was added

and the yellow soln. stirred at r.t. for 15 min. Then, **15a** (1.20 g, 3.50 mmol) in CH_2Cl_2 (300 ml) was added. After 3 h, H_2O (5 ml) was added, the soln. evaporated, and the remaining oil filtered over 40 g of Al_2O_3 with $CHCl_3$. CC (100 g of Al_2O_3, hexane/AcOEt 4:1) of the crude product afforded 1.64 g (68%) of **16d**. White solid. M.p. 88° (Et_2O/hexane). TLC (Al_2O_3, hexane/AcOEt 4:1): R_f 0.60. IR (KBr): 2980, 2925*w* (sat. CH); 1723*s* (C=O); 1596, 1564*m* (C=C); 1441*m*, 1364*m* (*t*-Bu ester); 1160*s* (C–O); 875*m*, 850*w*, 790*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.41, 1.43 (2*s*, 2 *t*-Bu); 2.60 (*s*, CH_3–C(6′)); 2.56–2.68 (*m*, 2 H–C(*β*), 2 H–C(*β*′)); 2.90–3.06 (*m*, 2 H–C(α), 2 H–C(α′)); 4.63 (*s*, CH_2Br); 4.87 (*s*, OCH_2–C(6″)); 4.89 (*s*, OCH_2–C(6)); 7.01 (*s*, H–C(5′)); 7.42 (*s*, H–C(5)); 7.45 (*d*, *J*(H–C(5‴), H–C(4‴)) = 7.8, H–C(5‴)); 7.59 (*d*, *J*(H–C(5″), H–C(4″)) = 7.8, H–C(5″)); 7.80, 7.87 (2*t*, *J* = 7.8, H–C(4″), H–C(4‴)); 8.04 (*s*, H–C(3′)); 8.17 (*s*, H–C(3)); 8.35, 8.37 (2*d*, *J* = 7.8, H–C(3″), H–C(3‴)). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.37 (CH_3–C(6′)); 28.06 ((CH_3)$_3$C); 30.48, 30.68, (C(*β*), C(*β*′)); 34.21 (CH_2Br); 35.82 (C(α), C(α′)); 73.89, 74.01 (CH_2OCH_2); 80.73 ((CH_3)$_3C$); 118.50, 120.03, 120.34, 121.21, 121.60, 123.35, 137.59, 137.86 (CH, arene); 155.05, 155.92, 156.16, 157.85, 157.91 (C, arene); 171.74 (C=O). Anal. calc. for $C_{38}H_{45}BrN_4O_5$ (717.67): C 63.59, H 6.32, Br 11.14, N 7.81; found: C 63.72, H 6.31, Br 11.38, N 7.82.

*Tetra(*tert*-butyl) 6,6″-{{4,4′-Bis{2-[(*tert*-butoxy)carbonyl]ethyl}-2,2′-bipyridine-6,6′-diyl}bis(methyleneoxymethlene)bis(2,2′-bipyridine-6′,6-diyl)bis(methyleneoxymethlene)}-6′,6‴-dimethylbis[2,2′-bipyridine]-4,4′,4″,4‴-tetraproprionate* (**5d**). A stirred soln. of **16d** (120 mg, 0.164 mmol) and **13d** (32 mg, 0.0669 mmol) in 60 ml of CH_2Cl_2/*t*-BuOH 1:1 was treated with KO(*t*-Bu) (19 mg, 0.167 mmol). After 24 h at r.t. (TLC: no starting material left), H_2O (1 ml) was added, the mixture evaporated, and the brown oil filtered over 10 g of Al_2O_3 with $CHCl_3$. Further purification by CC (100 g of Al_2O_3, hexane/AcOEt 4:1→2:1) gave 55 mg (47%) of **5d**. White solid. M.p. 108° (Et_2O/hexane). TLC (Al_2O_3, hexane/AcOEt 2:1): R_f 0.35. UV ($CHCl_3$): 290 (64200). FT-IR (KBr): 2975, 2928*m* (sat. CH); 1726*s* (C=O); 1596*s*, 1564*m* (C=C); 1438*m*, 1367*m* (*t*-Bu ester); 1146*s* (C–O); 848*m*, 788*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.41 (*s*, 3 *t*-Bu); 1.43 (*s*, 3 *t*-Bu); 2.59 (*s*, 6 H, CH_3–C(6′,6‴)); 2.56–2.67 (*m*, 12 H, 2 H–C(*β*,*β*″), 2 H–C(*β*′,*β*‴), 2 H–C(β^{VIII},β^{IX})); 2.90–3.06 (*m*, 12 H, 2 H–C(α,α″), 2 H–C(α′,α‴), 2 H–C(α^{VIII},α^{IX})); 4.88 (*s*, 8 H, CH_2–C(6,6″), CH_2–C(6^{VIII},6^{IX})); 4.90 (*s*, 8 H, CH_2–C(6^{IV},6^{VI}), CH_2–C(6^{V},6^{VII})); 7.01 (*s*, 2 H, H–C(5′,5‴); 7.43 (*s*, 4 H, H–C(5,5″), H–C(5^{VIII},5^{IX})); 7.68 (*d*, *J* = 7.7, 4 H, H–C(5^{IV},5^{VI}), H–C(5^{V},5^{VII})); 7.85 (*t*, *J* = 7.7, 4 H, H–C(4^{IV},4^{VI}), H–C(4^{V},4^{VII})); 8.05 (*s*, 2 H, H–C(3′,3‴)); 8.18 (*s*, 4 H, H–C(3,3″), H–C(3^{VIII},3^{IX})); 8.34 (*d*, *J* = 7.7, 4 H, H–C(3^{IV},3^{VI}), H–C(3^{V},3^{VII})). ^{13}C-NMR (50.3 MHz, $CDCl_3$): 24.49 (CH_3–C(6′,6‴)); 28.06 ((CH_3)$_3$C); 30.47, 30.68 (C(*β*,*β*″), C(*β*′,*β*‴), C(β^{VIII},β^{IX})); 35.84 (C(α,α″), C(α′,α‴), C(α^{VIII},α^{IX})); 73.89, 74.01 (CH_2OCH_2); 80.70, 80.84 ((CH_3)$_3C$); 118.39, 119.90, 120.48, 121.33, 123.45, 137.53, 151,36, 155.12, 155.52, 155.94, 156.23, 157.85, 157.94 (C of bpy); 171.56, 171.74 (C=O). FAB-MS (pos. mode): 1746.3 (calc. 1746.1). Anal. calc. for $C_{102}H_{124}N_{10}O_{16}$ (1746.09): C 70.16, H 7.16, N 8.02; found: C 70.20, H 7.14, N 7.93.

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